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Journal of Analytical Chemistry

TITANIUM CARBIDE IN PIG-IRON.*

BY P. W. SHIMER, EASTON, PA.

ON completing the filtration of a solution of pig-iron in hydrochloric acid, and after apparently everything had been transferred to the paper, a minute residue was observed remaining in the angle of the beaker in which the solution had been made. This residue had a steel-gray color and metallic luster and was hard and gritty when touched with a glass rod. Placed under a microscope and magnified 400 diameters, the substance was found to be made up almost entirely of opaque cubical crystals with some fragments having the same color and luster as the cubes. The appearance was strikingly like that of a collection of crystals of iron pyrites.

The amount of material obtained from ten to twenty grams of borings by solution in dilute hydrochloric acid, and careful decantation from graphite, was barely sufficient for a microscopic slide. A qualitative test of the minute amount of material obtained in this way, showed the presence of considerable titanium. After many fruitless trials by decantation and other methods, sufficient material for quantitative analysis was finally obtained in the following manner :

Two hundred and fifty grams of the coarsest possible turnings were dissolved in seven liters of hydrochloric acid of sp.

*[Read at the St. Louis meeting of the American Institute of Mining Engineers; communicated by the author.]

gr. 1.03. A solution by the aid of heat took four to five hours. It was allowed to settle, and the clear solution poured off. Great care was taken that none of the material which had settled to the bottom was lost. The graphitic residue was then completely transferred upon fine bolting-cloth, previously stretched and fastened over the top of a beaker. All graphitic lumps were broken up by the finger while directing a strong stream of water from a wash-bottle upon it. When all but the larger graphite scales had passed through, the bolting-cloth was removed. This treatment separates the larger particles of graphite, which are troublesome in the subsequent separation, gives the particles more nearly a uniform size, and sets free many of the minute crystals which are to be separated. A magnet was then moved about in the liquid until all magnetic particles were removed. The material thus separated from the iron under experiment was found to be interesting, as will be shown further on.

The residue was allowed to settle into the angle of the beaker, and the liquid carefully poured off. It was then ready for the separation.

An inclined plane of window-glass twelve feet long and five inches wide was arranged in two sections, each six feet long, placed end to end. Narrow strips of glass, one-half inch wide, were cemented to the sides and upper end of each section. Each section was cemented firmly to a perfectly straight board about six inches shorter than the glass. These pieces, with the glass overlapping about one inch, were supported at a convenient height above a long table. For the present separation it was found that a fall of one inch in the first section, and one-half inch in the second, answered the purpose very well. A large beaker of distilled water, with siphon and stopcock, was placed at the head of the inclined plane, and water allowed to drop slowly upon it. By means of a camel's-hair brush, the water was directed in a narrow stream, about one inch wide, throughout the whole length of the plane. Where the glass overlapped, a short glass rod was placed to lead the water to the lower section. At the end, the water was led into a beaker by means of a long glass rod. The

graphitic residue was then transferred to the head of the inclined plane with as little water as possible, and water allowed to drop slowly from the siphon.

The water at once begins to carry off the lighter and finer particles. It is necessary to keep tapping the residue with some convenient object, such as a platinum spatula, so as to prevent any graphite from being retained by the heavier crystals, and to keep the current flowing evenly over the whole residue. The separation soon becomes apparent, the graphite being carried forward faster than the heavier crystals.

At this stage it is necessary to remove with a magnet any remaining magnetic particles, since these interfere with the separation. When, after three or four hours, all the graphite had been washed from the inclined plane, the water was drained off and the residue allowed to dry. When dry, it formed a stream of bright metallic luster throughout the whole length of the plane. The material was then swept together and treated in a beaker with hot hydrochloric acid of sp. gr. 1.12, for the removal of a little iron. It was then again placed upon one of the sections of the inclined plane, and any remaining graphite separated from it. This second separation is not nearly so tedious as the first. Several separations of 250 grams each were made, and about one gram of pure material for analysis was obtained.

In the case of the iron under experiment it was necessary to have the turnings as coarse as possible. In this way the scales of graphite are not so much broken up, and more can be separated by the bolting-cloth. The crystals also are less broken. When fine borings were used it was not possible to get a satisfactory separation on the inclined plane; for the small particles, instead of being independent of each other, as when coarse borings are used, gathered together in little clumps enclosing the crystals sought, which were thus carried off and lost.

The solution and separation should also be made on the same day; for when a solution is allowed to stand longer than necessary to settle, there is a minute separation, perhaps of gelatinous silica, which interferes with the freedom of motion

of the particles, causing them to gather in clumps, as described.

In the case of another pig-iron on which some preliminary experiments were made, the substance to be separated was still more finely divided than in the present case. It was here found best to give little if any fall to the plane, and to regulate the separation by means of the current of water. Successful separations were made with an inclined plane only eight feet long.

A separation was also attempted upon a slowly revolving circular piece of glass two feet in diameter. The substance to be separated was placed in the center of the glass and water dropped slowly upon it. It was thought that the water would carry the graphite to the periphery of the glass, leaving the heavier crystals in the center. Only a little material could be separated in this way; but this result was plainly due to the fact that the glass used could not be made perfectly level. The great difference between the specific gravity of the crystals and graphite naturally suggests the usual separation by means of a dense solution; but the material is too finely divided for successful separation by this means.

The material separated on the inclined plane when deposited from water and dried has a brilliant luster and steel-gray color. When swept together the mass has a deep iron-gray color and little luster. The luster in the former case is due to the fact that, when allowed to deposit from water, the cubes arrange themselves unanimously with their faces upward, thus reflecting light uniformly.

On examining the material for analysis under the microscope, it was found to be free from graphite and to consist almost entirely of cubes, a large proportion of which were perfect. A few of the cubes had long handle-like projections from one of the angles. There were also occasional long slightly tapering nail-shaped crystals. The cubes varied in size from $\frac{1}{1500}$ to $\frac{1}{7000}$ of an inch (0.0169 to 0.0036 millimeter).

The material analyzed has a specific gravity of 5.10. It is insoluble in hydrochloric acid but readily soluble in nitric acid. The insolubility in hydrochloric acid explains how titanium in pig-iron is found and determined in the residue insoluble in this

acid. The solubility in nitric acid shows how the titanium is eliminated in the nitric and sulphuric acid method for the determination of silicon in pig-iron. It is apparently wholly unattacked by a strong boiling solution of caustic potassa. When ignited for several hours at a bright red heat in a current of hydrogen, it suffers no change of weight. The following is the analysis:

Titanium	71.58
Carbon	16.94
Iron.	3.77
Phosphorous.	0.69
Manganese	0.16
Sulphur.	1.57
Silicon	0.00
Nitrogen	0.00
Insoluble siliceous residue	1.09
Undetermined	4.20
	<hr/>
	100.00

The substance also contains a small undetermined amount of copper and vanadium, possibly in combination with sulphur. About 88 per cent. of the material is thus seen to be a titanium carbide in which titanium and carbon are present in very nearly the exact proportion of their atomic weights. The formula is therefore TiC . In the calculation 48 was used as the atomic weight of titanium. The slight excess of titanium may easily exist in other combination. This compound is probably new; for I have not been able to find mention anywhere of any simple compound of titanium and carbon. The iron and phosphorus in the analysis are due to an admixture of the difficulty-soluble phosphorus compound described below.

Determinations of titanium and carbon were made by various methods. In the first method, dry chlorine gas was passed at a red heat over the substance contained in a weighed porcelain boat. The volatile chlorides were passed through numerous bottles and bulbs containing water. Titanic acid was separated from this solution and purified in the usual way. The carbon remaining in the boat was burned in a current of oxygen after first being freed from chlorine by passing hydro-

gen over it at a red heat. In another analysis the substance was burned directly in oxygen, the carbon thus determined agreeing closely with the first determination. The residue remaining in the boat was fused with potassium bisulphate, and the titanous acid separated in the usual manner.

I have found cubical crystals like those described in every one of five or six pig-irons that I have examined, one of them being a sample of English Bessemer pig-iron marked Barrow No. 1; but in none were they so free from admixture of the nail-shaped and other crystals as in the iron under experiment. This iron was a fine sample of No. 1 foundry iron, having the following composition:

Phosphorus.	0.343
Silicon.	2.690
Sulphur.	0.047
Manganese.	0.594
Titanium.	0.203
Graphite.	3.664
Combined carbon.	0.111
Iron (by difference)	92.348
	<hr/>
	100.000

The titanium was determined in this iron by three different methods.

1. The residue insoluble in dilute hydrochloric acid was fused with potassium bisulphate, and the titanous acid separated in the well-known manner. The result was 0.199 per cent. titanium.

2. The residue insoluble in dilute hydrochloric acid was treated with nitric acid with the intention of dissolving out the titanium carbide—a method suggested by this investigation. The nitric acid solution was precipitated by ammonia, the precipitate filtered, washed and redissolved in dilute sulphuric acid, and the solution boiled after neutralizing excess of acid and adding sulphurous acid. The precipitate thus obtained was fused with sodium carbonate, extracted with water and filtered. The insoluble sodium titanate was dissolved in sulphuric acid and reprecipitated. The result was 0.206 per cent. titanium.

3. Dry chlorine gas was passed over the borings at a red heat, and led through bottles and bulbs containing water. The result by this method was 0.205 per cent. titanium.

It was found that in each of these three methods the first precipitates by boiling always contained phosphoric acid to such an extent as to cause very serious error when not separated. It was necessary, therefore, in each case to fuse the first precipitate with sodium carbonate and extract with water, thus separating soluble sodium phosphate from insoluble sodium titanate.

When properly carried out, the chlorine method certainly gives all the titanium in pig-iron. As much titanium was, however, found in the residue insoluble in hydrochloric acid by the first two methods as was found in the borings by the chlorine method. This proves that all the titanium, in this iron at least, is found in the residue insoluble in hydrochloric acid. It seems fair to conclude, then, that the titanium, instead of being uniformly dissolved in this iron, is mechanically disseminated through it in the form of a definite crystallized compound with carbon.

That part of the residue insoluble in dilute hydrochloric acid removed by the magnet was found to contain considerable phosphorus. It is not completely insoluble, even in very dilute hydrochloric acid, for on long boiling it dissolves. It is a finely divided granular substance, has a metallic luster, and is so brittle that it may readily be ground to dust in a mortar. It encloses considerable titanium carbide. Samples separated at different times contained phosphorus as follows: 10.32, 12.50 and 11.90 per cent. These varying results are due to varying conditions of time, temperature, and strength of acid. One of the samples contained 69.48 per cent of metallic iron. When only slightly heated, apparently not much above the boiling-point of water, partial oxidation takes place, a bright glow spreading over the whole mass. On further heating, the substance fuses easily. The compound appears to be completely insoluble in double chloride of copper and ammonium solution.

Duplicate determinations of the phosphorus remaining in-

soluble in a solution of the double chloride gave 0.155 and 0.158 per cent. phosphorus. That is, 45.63 per cent. of the total phosphorus in this iron remains in the insoluble residue in form of a high-phosphorus compound !

From the residue insoluble in dilute hydrochloric acid only about 12 per cent. of the total phosphorus could be separated by means of a magnet. I have not yet attempted a separation on the inclined plane of the residue insoluble in double chloride solution.

These notes on the phosphorus compound are only preliminary, for, owing to want of sufficient material, I have not been able to make a complete investigation of it.

I have great pleasure in acknowledging my indebtedness to Mr. Frank Firmstone of the Glendon Iron Works, who not only gave me the facilities of a large iron works, but greatly encouraged me by his interest in the progress of this investigation.

NOTES OF PRACTICAL WORK IN STATE LABORATORY, AUBURN, ALABAMA.

COMMUNICATED BY N. T. LUPTON,

Professor of Chemistry in the Agricultural and Mechanical College and State Chemist.

DETERMINATION OF NITROGEN IN COMMERCIAL FERTILIZERS BY B. B. ROSS AND L. W. WILKINSON, ASSISTANTS.

AT a meeting of official Agricultural Chemists held in Washington, September 1 and 2, 1885, the committee on nitrogen reported that the samples sent out by the committee were so few and meagre and the discrepancies so large as to make it inadvisable to recommend any method for the determination of nitrogen for use during the next season, and recommended that the entire report of the last committee be referred, without further action, to the next committee on ni-

trogen. The new committee, in accordance with the report referred to, sent out other samples during the present year with specific instructions to be followed in determinations according to the Ruffle method, the one proposed by the committee for adoption by the Association. Nitrogen was also determined in the same samples, for the purpose of comparison, by the soda-lime and the Kjeldahl methods. As these determinations were made with great care, the results are believed to be of sufficient interest to justify their publication.

The reagents used in the Ruffle method consisted of standard solutions of sulphuric acid and caustic potash, one-fourth normal; soda lime crushed, one-half in form of powder and one-half granular; Sodium Hyposulphite, commercial, fused, water-free, and powdered; finely powdered charcoal and flowers of sulphur, equal parts by weight; and cochineal solution as an indicator. The combustion tube was twenty inches in length and one-half inch in diameter.

The samples used for analysis were represented to consist of Nos. 1 and 2, ordinary commercial fertilizers containing nitrogen, No. 3, a rather superior sample of cotton seed meal, and No. 4, a nitrate mixed with sugar.

Careful analyses of the chemicals used in the Ruffle method showed them to contain a small percentage of nitrogen which is allowed for in the following results:

RESULTS ACCORDING TO THE RUFFLE METHOD.

	(a)	(b)	(c)	Average.
Sample No. 1—Nitrogen found . . .	1.83½	1.86	1.85	1.8483
" " 2 " " . . .	2.15	2.16¼	2.15	2.1541
" " 3 " " . . .	7.66½	7.57½	7.35	7.53
" " 4 " " . . .	3.45	3.39½	3.35	3.3983

RESULTS ACCORDING TO THE METHOD WITH SODA LIME.

	(a)	(b)	(c)	Average.
Sample No. 1—Nitrogen found . . .	1.84	1.85		1.845
" " 2 " " . . .	2.05	2.12½		2.0875
" " 3 " " . . .	7.25	7.27½		7.2625
" " 4 " " . . .	2.10	2.12½		2.0875

RESULTS ACCORDING TO THE KJELDAHL METHOD.

					(a)	(b)	(c)	Average.
Sample No. 1—Nitrogen found. . .					1.85			
" " 2 " " . .					2.17½			
" " 3 " " . . .					7.33			
" " 4 " " . . .								

From eight to ten hours digestion with sulphuric acid was required in the Kjeldahl method and about three-quarters of an hour for distillation, making it long and tedious. No. 4, consisting of sodium nitrate and sugar, yielded totally unreliable results, and is omitted. The quantity of material sent was too small to allow of other determinations.

The above determinations show the uniform and satisfactory results obtained by the Ruffle method, and commend it to the favorable consideration of agricultural chemists especially.

ON THE ACTION OF HYDROFLUORIC ACID ON SILICA AND SILICATES.*

BY J. B. MACKINTOSH.

In a preliminary note on this subject published in July,† I called attention to the great difference in the behaviour of quartz and opal, when submitted to the action of hydrofluoric acid, and gave a general indication of the behaviour of silicates, under similar circumstances. The few data contained in the above mentioned note will all be included in the present paper, which I hope may be regarded as an acceptable contribution to the literature of the silicates.

The starting point of the present investigation arose from a question which occasionally presented itself in the course of my professional work. I have frequently been appealed to, to decide on the identity of cut and polished gems, without, of

*Read before the American Chemical Society, Nov. 5, 1886; communicated by the Author.

†School of Mines Quarterly No. 4, Vol. 7.

course, subjecting them to injury in any way. Chemical analysis being out of the question it is necessary to make the determination by means of the physical characteristics alone, but in certain cases it becomes a very difficult matter to decide. The two gems garnet and spinel occurring in varying shades of color, although generally readily distinguished, yet occasionally approach so closely in their characteristics that I attempted to find a means of differentiation based on their chemical constitution, which while it would have the certainty of a qualitative analysis, would leave the gem practically uninjured. The composition of spinel being a compound of a protoxide with a sesquioxide in equal molecular proportions, while that of garnet is a silicate which may be regarded as derived from spinel by the substitution of an equivalent amount of silica for two-thirds of the sesquioxide present, it seemed probable that hydrofluoric acid would furnish the means of differentiation sought for, but on making the experiment it was found that neither mineral was attacked in the slightest degree. This unexpected result was so interesting that I determined to extend the investigation further than I had originally purposed and to examine in this way the principal silicates occurring in nature.

The following tables show the results of the qualitative experiments I have made. I have included in these tables the atomic formulæ, the specific gravity, the unit volume and the percentage of silica in the mineral. For the first three data I am indebted to Dr. T. Sterry Hunt and have taken most of them from his recently published work on "A Natural System of Mineralogy."*

The atomic formulæ are those employed by Sterry Hunt and differ from ordinary formulæ, in that the quantities represented by the symbols of the element are all equivalent to one atom of hydrogen. The coefficients thus represent the oxygen ratios of the constituents, and the formulæ are very much simplified.

*A Natural System of Mineralogy with a Classification of the Native Silicates, by Thomas Sterry Hunt. S. E. Cassino, Boston, Mass.

MINERALS WHICH ARE VISIBLY ETCHED BY HYDROFLUORIC ACID.

	ATOMIC FORMULA.	SP. GR.	VOLUME.	PER CT. SiO_2	REMARKS.
Quartz.	Si_2O_2	2.67	5.62	100.	Very slightly attacked
Opal	Si_2O_2	2.2	6.81	100.	H_2O regarded as non-essential.
Petalite	$(\text{Li}_2\text{Al}_2\text{Si}_2)\text{O}_{20}$	2.42	6.33	78.	
Wollastonite	$(\text{Ca}_2\text{Si}_2)\text{O}_8$	2.92	6.62	51.7	
Rhodonite.	$(\text{Mn}_2\text{Si}_2)\text{O}_8$	3.63	6.06	46.7	
Tremolite	$[(\text{Mg}_2\text{Ca}_2)\text{Si}_2]\text{O}_8$	2.97	5.88	57.4	Very slightly attacked.
Willemite	$(\text{Zn}_2\text{Si}_2)\text{O}_8$	4.18	6.63	27.5	
Chrysolite.	$(\text{Mg}_2\text{Si}_2)\text{O}_8$	3.40	5.38	45.	
Fayalite.	$(\text{Fe}_2\text{Si}_2)\text{O}_8$	4.35	5.86	27.3	Very slightly attacked.
Wernerite	$(\text{M}_2\text{Al}_2\text{Si}_2)\text{O}_{20}$	2.70	6.44	48.5	
Vesuvianite	$(\text{Ca}_2\text{Al}_2\text{Si}_2)\text{O}_{10}$	3.40	5.67	37.	Very slightly attacked.
Biotite	$(\text{Mg}_2\text{Al}_2\text{Si}_2)\text{O}_{10}$	3.00	6.06	41.	Very slightly attacked.
Phlogopite	$(\text{Mg}_2\text{Al}_2\text{Si}_2)\text{O}_{10}$	2.85	6.35	40.	Very slightly attacked.
Iolite	$[(\text{Mg}_2\text{Fe}_2)\text{Al}_2\text{Si}_2]\text{O}_8$	2.67	6.31	49.	
Albite	$(\text{Na}_2\text{Al}_2\text{Si}_2)\text{O}_{10}$	2.62	6.24	68.6	
Orthoclase.	$(\text{K}_2\text{Al}_2\text{Si}_2)\text{O}_{10}$	2.54	6.83	64.6	
Oligoclase	$[(\text{Na}_2\text{Ca}_2)\text{Al}_2\text{Si}_2]\text{O}_{10}$	2.65	6.27	61.5	
Labradorite	$[(\text{Ca}_2\text{Na}_2)\text{Al}_2\text{Si}_2]\text{O}_{10}$	2.70	6.28	55.5	
Leucite	$(\text{K}_2\text{Al}_2\text{Si}_2)\text{O}_{10}$	2.56	7.09	55.	
Titanite	$(\text{Ca}_2\text{Si}_2\text{Ti}_2)\text{O}_8$	3.50	5.65	30.5	
Datolite	$(\text{Ca}_2\text{Si}_2\text{B}_2\text{H}_2)\text{O}_{10}$	2.99	5.35	37.5	Very slightly attacked.
Pectolite.	$(\text{Ca}_2\text{Si}_2)\text{O}_{17} + 1\text{aq}$	2.78	6.57	54.6	
Apophyllite	$(\text{Ca}_2\text{Si}_2)\text{O}_8 + 2\text{aq}$	2.35	6.44	53.	
Calamine	$(\text{Zn}_2\text{Si}_2)\text{O}_8 + \frac{1}{2}\text{aq}$	3.50	6.87	25.	
Prehnite.	$(\text{Ca}_2\text{Al}_2\text{Si}_2)\text{O}_{11} + 1\text{aq}$	2.95	5.64	43.6	Etched with difficulty.
Heulandite	$(\text{Ca}_2\text{Al}_2\text{Si}_2)\text{O}_{18} + 5\text{aq}$	2.20	6.58	59.	
Stilbite	$(\text{Ca}_2\text{Al}_2\text{Si}_2)\text{O}_{18} + 6\text{aq}$	2.20	6.46	57.4	
Harmotome	$(\text{Ba}_2\text{Al}_2\text{Si}_2)\text{O}_{10} + 5\text{aq}$	2.45	6.82	46.5	
Chabazite	$(\text{Ca}_2\text{Al}_2\text{Si}_2)\text{O}_{13} + 6\text{aq}$	2.19	6.41	52.2	
Analcite	$(\text{Na}_2\text{Al}_2\text{Si}_2)\text{O}_{12} + 2\text{aq}$	2.29	6.86	54.5	
Natrolite	$(\text{Na}_2\text{Al}_2\text{Si}_2)\text{O}_{10} + 2\text{aq}$	2.25	7.03	47.3	
Serpentine	$(\text{Mg}_2\text{Si}_2)\text{O}_7 + 2\text{aq}$	2.53	5.78	42.	
Halloysite.	$(\text{Al}_2\text{Si}_2)\text{O}_7 + 3\text{aq}$	2.40	5.75	43.3	
Jeffersite	$[\text{Mg}_2\text{Al}_2\text{Fe}_2\text{Si}_2]\text{O}_{20} + 7\frac{1}{2}\text{aq}$	2.30	6.50	34.	

MINERALS WHICH ARE NOT VISIBLY ETCHED BY HYDROFLUORIC ACID.

	ATOMIC FORMULA.	SP. GR.	VOLUME.	PER CT. SiO_2	REMARKS.
Quartz	Si_2O_2	2.67	5.62	100	Some varieties.
Enstatite	$(\text{mg}_1\text{si}_2)\text{O}_3$	3.10	5.54	60	
Diopside	$[(\text{mg ca})_1\text{si}_2]\text{O}_3$	3.28	5.48	54	
Spodumene	$(\text{li}_1\text{al}_2\text{si}_2)\text{O}_{12}$	3.18	4.88	64	
Beryl	$(\text{be}_2\text{al}_2\text{si}_2)\text{O}_{12}$	2.70	5.52	67	
Tremolite	$(\text{mg}_{2.4}\text{ca}_{1.6}\text{si}_2)\text{O}_3$	2.97	5.88	57.4	Slightly attacked by long exposure.
Zircon	$(\text{zr}_1\text{si}_1)\text{O}_2$	4.70	4.84	33	
Garnet	$(\text{ca}_1\text{al}_1\text{si}_2)\text{O}_4$	3.50	5.37	36	
Epidote	$(\text{ca}_1\text{al}_{1.5}\text{fi}_{1.5}\text{si}_2)\text{O}_3 + \frac{1}{3}\text{aq}$	3.40	5.40	38	
Zoisite	$(\text{ca}_1\text{al}_1\text{si}_2)\text{O}_3$	3.35	5.32	44	
Axinite	$(\text{ca}_1\text{al}_{1.5}\text{fi}_{1.5}\text{b}_{1.5}\text{si}_{1.5})\text{O}_7$	3.27	5.53	44	
Danburite	$(\text{ca}_1\text{b}_1\text{si}_2)\text{O}_3$	3.00	5.12	48	
Lepidolite	$(\text{m}_1\text{al}_{1.5}\text{si}_2)\text{O}_{12} + \frac{1}{2}\text{aq}$	3.00	5.61	46.5	
Muscovite	$(\text{k}_1\text{al}_2\text{si}_2)\text{O}_{12}$	3.12	5.68	46.5	
Biotite	$[\text{m}_1(\text{alfi})_2\text{si}_2]\text{O}_{12}$	3.00	6.06	41	Very slightly attacked.
Phlogopite	$(\text{m}_1\text{al}_2\text{si}_2)\text{O}_{12}$	2.85	6.35	40	Very slightly attacked.
Fayalite	$(\text{fe}_1\text{si}_1)\text{O}_2$	4.35	5.86	27.3	Very slightly attacked.
Tourmaline	$(\text{m}_1\text{al}_2\text{si}_2)\text{O}_3$	3.05	5.36	37.5	
Andalusite	$(\text{al}_2\text{si}_2)\text{O}_3$	3.35	4.83	37.5	
Cyanite	$(\text{al}_2\text{si}_2)\text{O}_3$	3.66	4.42	37.5	
Topaz	$(\text{al}_2\text{si}_2)\text{O}_4\text{f}_1$	3.65	5.04	34	
Datolite	$(\text{ca}_2\text{si}_2\text{b}_2\text{O}_3 + \text{Iaq})$	2.99	5.35	37.5	Forms coating of Ca F.
Prehnite	$(\text{ca}_2\text{al}_2\text{si}_2)\text{O}_{12} + \text{Iaq}$	2.95	5.64	43.6	Slightly attacked.
Talc	$(\text{mg}_2\text{si}_{10})\text{O}_{14} + \text{Iaq}$	2.60	6.07	62.8	
Ripidolite	$(\text{ng}_2\text{al}_2\text{si}_2)\text{O}_{14} + 4\text{aq}$	2.77	5.70	31.3	
Margarite	$(\text{ca}_1\text{al}_2\text{si}_2)\text{O}_{11} + \text{Iaq}$	2.99	5.54	30	

To the above may also be added the non-silicates corundum, spinel and chrysoberyl which are not attacked, and the artificial product glass, which is.

I have included in both classes several species which seem to be on the border line, and which sometimes seem to be unattacked, while at other times by longer exposure or by treatment of a different surface a slight action becomes evident.

Thus with vesuvianite, the prism faces of a crystal showed no etching, while the basal plane of the same crystal was perceptibly attacked ; this, however, might have been due to a difference in the time of exposure, though in other cases, as in quartz, it is undoubtedly the fact that some surfaces are not attacked as readily as others.

By inspection of the data given it will be seen that the amount of silica present does not determine the action of the acid, nor does the molecular ratio of silica to the bases, but we see that the volumes show a very decided difference. In the non-attacked species, the volume for the greater number is considerably below 6, while in the non-resisting species it is generally considerably above this figure. Thus comparing enstatite and diopside with wollastonite and tremolite, we have in the first two volumes of 5.54 and 5.48, in the less dense wollastonite the volume is 6.62 while the tremolite has an intermediate volume of 5.88 and it is likewise intermediate in its relation to the acid. These four minerals differ in composition mainly by the gradual substitution of lime for magnesia, the ratio of bases to silica remaining unchanged. It is possible that the nature of the base may have a considerable effect on the extent of condensation of the molecule. In the above instances the replacement of magnesia by lime seems to tend to increase the volume and decrease the resisting power to HF.

At the suggestion of Dr. T. Sterry Hunt, while carrying on these qualitative tests, I also proceeded to make quantitative comparisons of several minerals, using quartz as a standard of reference, but I immediately found it was so slightly attacked that it would not do for the purpose.

In these experiments the minerals were reduced to an average size of 3-100 cubic millimeter by careful sizing, and one gram of each sample was taken for each experiment. The samples were all treated for an hour with an excess of dilute hydrofluoric acid (9 per cent.) at the ordinary temperature of the laboratory, all conditions being as far as possible the same ; at the expiration of that time the acid was poured off, the residues carefully washed and dried and where any

insoluble fluorides or silica resulting from the decomposition of the mineral were present, they were removed by the use of a fine bolting-cloth, before weighing the residue of unattacked mineral. The results obtained are given in the following table which also shows the atomic formula, the density, the volume and the per cent. SiO₂ for each mineral:

QUANTITATIVE RESULTS.

	ATOMIC FORMULA.	SP. GR.	VOLUME.	PER CT. SiO ₂	PER CT. DISSOLVED	
Quartz.	si ₁ o ₁	2.67	5.62	100	1.56	
Tremolite . . .	(mg ₃ ,ca ₁ ,si ₃)o ₈	2.97	5.88	57.4	2.47	Gouverneur, N. Y.
Augite		3.30			2.61	} Note 1.
Hornblende . .		3.21			2.64	
Chrysolite . . .	(mg ₁ si ₁)o ₂	3.40	5.38	45	5.40	
Prehnite. . . .	(ca ₂ al ₂ si ₂)o ₁₁ +1aq	2.95	5.64	43.6	8.59	Paterson, N. J.
Albite.	(na ₁ al ₁ si ₂)o ₂₈	2.62	6.24	68.6	23.1	
Labradorite . .	(ca ₇ ,na ₁ ,al ₁ si ₂)o ₁₀	2.70	6.28	55.5	24.65	Note 2
Petalite	(li ₁ al ₁ si ₂)o ₂₈	2.42	6.33	78	28.97	Sweden.
Oligoclase . [(hca) ₁ ,na ₁ ,al ₁ si ₂]o ₂₄		2.61	6.41	64.2	35.25	Haddam, Conn.
Orthoclase. . .	(k ₁ al ₁ si ₂)o ₁₈	2.54	6.83	64.6	43.45	Pike's Peak, Col.
Iolite	(mg ₇ ,fe ₁ ,al ₁ si ₂)o ₈	2.67	6.31	49	47.34	Finland, Note 3.
Oligoclase . . .	(na ₇ ,ca ₁ ,al ₁ si ₂)o ₁₂	2.65	6.27	61.5	50.83	
Nephrite? . . .					61.59	Easton, Pa , Note 4.
Leucite	(k ₁ al ₁ si ₁)o ₁₂	2.56	7.09	55	66.30	
Rhodonite. . .	(mn ₁ si ₂)o ₈	3.63	6.06	46.7	69.21	Franklin, N. J.
Opal	si ₁ o ₁	2.2	6.81	100	77.28	
Serpentine. . .	(mg ₂ si ₄)o ₇ +2aq	2.53	5.78	42	80.67	
Halloysite . . .	(al ₂ si ₄)o ₇	2.40	5.75	43.3	100	Lookout, Note 5. Ala.
Willemite . . .	(zn ₁ si ₁)o ₂	4.18	6.63	27.5	100	Franklin, N. J.

Two samples of willemite were also treated for 15 minutes with the following results :

- Green willemite, massive 86.78
- Brown willemite, crystallized (troostite) . . 92.09

NOTE 1. These samples of augite and hornblende are from Teplitz, Bohemia. I have not their analysis.

NOTE 2. The surfaces of the grains were coated with a white

incrustation, probably of fluoride of calcium, which would both retard the action of the acid, and make the apparent amount dissolved less than the truth, both causes of error acting in the same direction.

NOTE 3. A fine powder insoluble in HF was formed—either an insoluble fluoride or an included mineral.

NOTE 4. This so-called Nephrite, said to be a variety of amphibole, is from Easton, Pa. Dana says it is a mixture of minerals. The result I have obtained shows that it is certainly not amphibole, nor does it contain much, if any, of that species.

NOTE 5. This disintegrated with great rapidity, but left an insoluble residue behind, either an insoluble product of the reaction or an included mineral.

Now on comparing together minerals of like formula in this table, we will see that the one with least volume is likewise least attacked by the acid, for instance, quartz and opal, tremolite and rhodonite, chrysolite and willemite, albite and orthoclase. Taking together the different feldspars and minerals of analagous composition, although they are not strictly comparable on account of the variation in the amount of silica, we have the series in order of solubility: Albite, labradorite, petalite, oligoclase orthoclase, oligoclase, leucite, which, with the exception of the second oligoclase, is also the order of increase of volume. It is of course to be expected that variations in composition will have a great influence in modifying the action of the acid, but oligoclase seems to be exceptional, as it is intermediate in composition between albite and labradorite, and we would expect its solubility to be between them also.

The oligoclase which gave me a solubility of 50.83 per cent. was from a Swedish locality, but I could not obtain its analysis. On account of the discrepancy in this result with what we should expect, I obtained from Prof. B. W. Frazier, of Lehigh University, a sample of oligoclase from Haddam, Conn., (the first one in the table), which gave a solubility of

35.25 per cent.—a specific gravity of 2.61 and a volume of 6.41. The analysis of oligoclase from this locality leads to an atomic formula differing slightly from that given by Dr. Hunt, but agreeing with that given by Dana. This result takes its place in the proper order according to volume, and I think leaves no doubt that the volume accorded to the 50.83 per cent. oligoclase is erroneous. This experiment was made at a different time, and under slightly different conditions, so that the solubility found is probably rather less than it should be.

To further illustrate the subject, I obtained a sample of slag from an iron cupola-furnace, the outside portion being vitreous from sudden cooling while the interior was opaque and crystalline. The composition of the two portions being presumably the same, as the piece chosen was but the size of a fist, any variation in solubility could only be ascribed to the molecular condition, and not to any difference of composition. The crystalline portion was very porous, it having an apparent specific gravity in the lump of 2.34, but on pulverizing finely, though not to an impalpable powder, the density rose to 2.97. The vitreous portion changed less—from 2.77 in lump to 2.81 in powder.

The results obtained for solubility in 9 per cent. fluorhydric acid were

	SP. GR.	VOLUME RATIO.	PER CT. DISSOLVED.
Vitreous slag . . .	2.81	1.057	68.80
Crystalline slag . .	2.97	1.	9.60

This result also agrees perfectly with what might be expected.

M. W. Iles in a paper on The Decomposition and Analysis of Slags* describes a method of obtaining samples of slags for analytical purposes by chilling the melted slag suddenly, thus obtaining a vitreous sample, which is readily soluble in dilute hydrochloric acid; while if allowed to cool and become crystalline it is not attacked by the acid. This is a practical ap-

*School of Mines Quarterly, Vol. 5, p. 351.

plication of the law of increase of solubility with increase of volume set forth by Sterry Hunt in 1863, when he asserted in comparing the silicates meionite and zoisite that "the augmentation of hardness, of density, and of chemical indifference which is seen in this last species is doubtless to be ascribed to a more elevated equivalent; or, in other words, to a more condensed molecule." Again in 1867, he wrote, after naming a number of groups of related minerals: "The hardness of these isomeric or allotropic species, and their indifference to chemical reagents, increases with their condensation; or, in other words, varies inversely as their empirical equivalent volume, so that we here find a dual relation between chemical and physical properties." This is resumed in his concise statement that "in related and homologous species, the hardness and chemical indifference are inversely as the value of V ." (the so-called atomic volume; or, in other words, that they increase with the diminution of V .)* The specific gravity of solids and liquids is, according to Sterry Hunt, a function of their equivalent weights.

In order to test still further the truth of this law, I ignited several samples of the granulated quartz, used in the previous experiments, for varying periods of time, anticipating that the longer the period of ignition, the greater would be the solubility, since we know that fused quartz has a lower specific gravity than the original crystal. The results were extremely satisfactory, and are as follows:

INFLUENCE OF IGNITION ON THE SOLUBILITY OF QUARTZ.

1 Gram of each sample treated for 1 hour with excess of dilute (9 per cent.) HF.

	PER CT. DISSOLVED.	SP. GR.
Raw Quartz	2.18—1.28	2.64
Same, ignited over Bunsen burner, 30 minutes	1.61	
" " " " " 45 "	1.78	
" " " " " 75 "	1.87	
" " " " " 120 "	2.15	
" " " " " 75 " and over Blast lamp 45 minutes	4.23	2.62
Same, ignited over blast lamp 120 minutes.	2.79	
" " " " " 210 "	5.35	
Fused Quartz	11.02	2.22

* Comptes Rendus de l'Academie des Sciences, lvi. 1256; Hunt's Chemical and Geological Essays, p. 446, 457, and Mineral Physiology and Physiography, p. 304.

I obtained the sample of fused quartz through the kindness of Dr. T. Sterry Hunt, who prepared it for the electrical furnace of the Messrs. Cowles, at Cleveland, Sept. 1st, 1885.* The sample taken was treated for an hour and a quarter at the same time as a sample of ordinary quartz for comparison. In that time it had lost 13.77 per cent., against 2.13 per cent. for the raw quartz. In the table I have deducted one-fifth this amount, so as to give the solubility in one hour, which permits direct comparison with the other determinations. The solubility of the raw quartz, I find varies in different determinations. I have in all, obtained the following values, 1.28, 1.56, 1.70, 1.70 and 2.18; the last figure is probably too high from mechanical loss.

Although the temperature of ignition is far too low to effect fusion, the results show that a molecular change has commenced towards the less dense and more easily soluble form of silica. In this connection, I attempted to prepare some tridymite by the fusion of amorphous silica with metaphosphate of sodium, and obtained thin plates which were readily soluble in the acid. I had not enough material to make other than the one test, and only surmise that it really was tridymite, though probably an impure sample.

The action of quartz being so interesting, I made several experiments on whole crystals of different crystalline modifications, from three localities, in order to ascertain the quantitative differences between them, since I had noticed in my qualitative tests that some quartz crystals did not show any appreciable etching action. As in these cases the amount of action depends on the surface exposed, I have measured the area of exposed faces, protecting broken surfaces, and certain faces, with wax, unless otherwise mentioned. (See table on next page.)

With opal, the figure given as expressing the amount dissolved per square centimeter is necessarily lower than the truth, as the area of the exposed surface diminishes as the solvent action progresses. In the present case, the area at the

* Transactions of the American Institute of Mining Engineers, Vol. XIV, p. 492.

CRYSTALS OF QUARTZ.

TREATED FOR 1 HOUR IN 9 PER CENT. HYDROFLUORIC ACID.

	LOCALITY.	WEIGHT GRAMS.	AMOUNT DISSOLVED.		AREA OF FACES SQUARE CENTI- METERS.	AMOUNT DISSOLVED PER SQUARE CENTIMETER GRAMS.	REMARKS.
			TOTAL.	PER CT.			
Quartz crystal. .	Herkimer, N. Y.	0.5742	0.0002	0.035	1.5	0.000133	Not visibly etched. Approximate- ly same size.
Opal.	?	0.4005	0.1140	28.46	1.5	0.076	

TREATED FOR 1 HOUR IN 54PER CENT. HYDROFLUORIC ACID.

LOCALITY.	WEIGHT GRAMS.	AMOUNT DISSOLVED.		AREA OF FACES		AMOUNT DISSOLVED PER SQ. CM.—GRAMS	REMARKS.
		TOTAL.	PER CT.	SQ. CM.	PER SQ. CM.		
Herkimer, N. Y. .	0.9733	0.0004	0.041	2.2		0.000182	Not visibly etched, perfect crys- tal completely exposed. Visibly etched, fractured sur- face also exposed. Visibly etched, acute rhombohe- dral faces exposed. Visibly etched, prism faces ex- posed.
White Plains, N. C .	0.6805	0.0016	0.235				
White Plains, N. C .	6.5827	0.0024	0.036	7.2		0.000333	
Hot Springs, Ark. .	22.0087	0.0050	0.023	11.9		0.000446	

end of the experiment is only about 80 per cent. of the area at the commencement, so that the loss per square centimeter will be somewhere between 0.095 and the figure given. The quartz crystal was without flaw, and was exposed on all faces. It did not show the slightest dimming of its brilliancy, and were it not for other experiments, it would be difficult to believe that the loss observed was not due to errors of experiment solely.

These figures show a quite decided, though small difference of susceptibility in the crystals from different localities. In the first "White Plains, N. C." specimen, the amount dissolved was relatively larger than in any of the others, but this is due to the exposure of the fractured surface, which is far more readily attacked than the natural faces, as the following experiment will show.

Action on polished sections of quartz cut perpendicularly to the axis of the crystal.

POLISHED SURFACES.

Treated for 1 hour in 54 per cent. HF.

TOTAL AREA EXPOSED SQUARE CENTIME- TERS.	WEIGHTS GRAMS.	AMOUNT DISSOLVED.		AMOUNT DISSOLVED PER SQUARE CM. —GRAMS.
		TOTAL.	PER CT.	
13.73	2.5242	0.0575	2.28	0.0042
15.24	2.2259	0.0778	3.49	0.0051
12.46	6.3890	0.0540	0.84	0.0043

In the last case, the natural faces of the crystal formed the sides of the section, and if we exclude them from our calculations, the area of the cut surfaces will be 8.46 sq. cm. and the amount dissolved per square centimeter of cut surface will be 0.0064. Here we see that the rate of attack is from 10 to 30 times faster than on the natural faces.

The etched surfaces of quartz crystals show a very peculiar variety of markings. Irregular and curved hair lines, having apparently no relation to the crystallographic form, are found in some places; the twinning structure is also developed, showing the complex nature of the crystal. On artificial surfaces of quartz the twinning structure is made very evident. In 1852–1855 F. Leydolt* made a series of experiments on quartz

* Eine neue Methode die Achate, und andere quarzhaltige Mineralien naturgetreu darzustellen, Jahrb. d. K. K. geologischen Reichsanstalt, II, Jahrgang 2, S. 124.

and agates with hydrofluoric acid, and says: "I am led to believe that agates are composed of layers of different chemical constitution, or at least in a different state of aggregation. Quartz crystals preserve their brilliant surface and are not dissolved." He also says:† "The feldspar is dissolved, while the quartz remains quite unaltered," and again "wood opals and other quartzose stones show differences in constitution."

The action of hydrofluoric acid on different silicates has already been utilized as a means of purification‡ and for the proximate analysis of rocks,|| but so far as I am aware, it has only been used to separate the insoluble or difficultly soluble minerals from the readily soluble ones with which they are associated. From the quantitative results presented in this paper, it will be readily seen how it may be applied to determine the nature of a mineral; to distinguish for instance between the different feldspars. It would also be possible to arrive quickly at the approximate composition of a rock of which the constituent minerals were known, such as a syenite or granite. When used in conjunction with Thoulet's solution, complex mixtures of minerals may be readily determined. I applied the acid to determine whether a specimen of cassiterite and quartz was only a mixture of the two minerals or a silicate of tin as was claimed for it by its European label. I obtained a residue of pure SnO_2 , practically the whole amount present, which probably would not have been the case if it had been a compound.

Of course, the figures given in the present paper only apply to the circumstances under which the experiments were carried on; it is possible that with a different degree of comminution or with a different strength of acid, the rate of attack might be different, so that each investigator would need to construct a table of solubilities suited to the circumstances under which he works.

Many analytical processes have been proposed, and used,

† Loc. cit. S. 126.

‡ Treatment and Qualitative Composition of Zircon. Ed. Linnemann, Chem. News, p 233, Vol. LII, 1885.

|| Mineralogie Micrographique, F. Fouque et Michel Levy, Paris, 1879, p. 116, and T. Sterry Hunt, Mineral Physiology and Physiography, p. 214.

either for the decomposition of silicates by hydrofluoric acid, or for the determination of fluorine by conversion into silicon fluoride. Now it is plain that in the latter case, quartz is about the worst material we can introduce to furnish the necessary silica, and in the former case that we cannot depend on the complete decomposition of a silicate by simple treatment with hydrofluoric acid.

In conclusion I desire to acknowledge my indebtedness to Dr. T. Sterry Hunt for many suggestions which he has made and information given during the course of my experiments ; to Dr. T. Eggleston for his kindness in furnishing me with most of the material for the investigation, and to Prof. B. W. Frazier and Mr. G. F. Kunz, for assistance in procuring special specimens.

NOTE ON STILLWELL'S METHOD OF OPIUM ANALYSIS.

BY L. D. GODSHALL.

Mr. C. M. Stillwell (Amer. Chem. Jour. 8, 295) has proposed a method for the analysis of Opium, which is for the most part a modification of the method of Squibb. The chief novelty in the method consists in the use of saturated solutions of morphia for washing the crystals. My friend, Mr. E. Luttgen, chemist for Keasbey & Mattison, has, at my suggestion, kindly compared this method with the one in use there (a modification of the method laid down in the U. S. P.) with the following results:

Method of Keasbey & Mattison(a)	. .	9.95 per cent.
“ “ “ “ (b)	. .	10.00 “
Stillwell's Method	10.05 “

Judging from this single comparison the method seems to be an accurate one. The only objection that suggests itself is that it is rather tedious. One point in connection with the method needs emphasis, viz., to conduct the evaporation in a shallow dish, as rapidly and at as low a temperature as possible, as otherwise morphia may be destroyed.

TYROTOXICON: ITS PRESENCE IN POISONOUS CHEESE, ICE-CREAM AND MILK.¹

BY VICTOR C. VAUGHAN.

I. POISONOUS CHEESE.

Historical.—The learned poet and chemist, Justinus Kerner, first made experimental investigations concerning the nature of certain foods which become poisonous by fermentation, or more properly by putrefaction. Kerner's first work was published in 1817². This was devoted to poisonous sausage, and in this work we find that the author concluded that the poisonous principle consisted of a fatty acid analogous to the sebatic acid of Thenard. Later, Kerner modified this opinion and announced his belief that the poisonous substance consisted of a fatty acid combined with a volatile base³. Dann following Kerner believed the active principle of poisonous sausage to be an acrid, empyreumatic oil, which when pure is not poisonous, but is rendered so by combination with fatty acids⁴. Buchner describes a botulinic acid which he conceived to be the active agent. Other observers also attributed the poisonous effects to fatty acids.

These statements in regard to poisonous sausage have been made on account of the similarity of the effects of poisonous sausage and poisonous cheese, and to call attention to the general belief of the older investigators that the active agent was in some way intimately connected with the fatty acids.

In 1827, Professor Hünnefeld made some analyses of poisonous cheese, and experimented with extracts upon the lower animals⁵. He accepted the ideas of Kerner in a somewhat modified form, and thought the active agents to be caseic and sebatic acids. About the same time, Sertürner making some

¹ Read before the Chemical Section of the American Association for the Advancement of Science, August, 1886. Communicated by the author.

² Das Fettgift oder die Fettsaeure und ihre Wirkungen auf dem Thierischen Organismus, &c. Stuttgart und Tubingen, 1817. Hiller gives the date of Kerner's first paper as 1782, but Kerner was not born until 1786.

³ Die Neuste Vergiftungen durch Verdorbene Wuerste, &c., Carlsruhe, 1821.

⁴ Horn's Archiv, 1828, B, 1. S. 596.

⁵ Horn's Archiv, 1827, B. 1, S. 203.

analyses of poisonous cheese for Dr. Westrumb, also traced the active agents, as he supposed, to sebacic and caseic acids¹. We see from the above that during the first part of the present century, the fatty acid theory, as we now call it, was generally accepted.

In 1844, Dr. Christison, after referring to the work of Hünnefeld and Sertürner, makes the following statement: "His (Hünnefeld's) experiments, however, are not quite conclusive of the fact that these fatty acids are really the poisonous principles, as he has not extended his experimental researches to the caseic and sebacic acids prepared in the ordinary way. His views will probably be altered and simplified if future experiments should confirm the late inquiries of Braconot, who has stated that Proust's caseic acid is a modification of the acetic combined with an acrid oil."²

In 1852 Schlossberger made experiments with the pure fatty acids and demonstrated their freedom from poisonous properties.³ These experiments have been verified repeatedly, so that now it is well known that all the fatty acids obtainable from cheese are devoid of poisonous properties.

It may be remarked here that there is every probability that the poisonous substance was present in the extracts obtained by the older chemists. Indeed, we may say that this is a certainty, since the administration of these extracts to cats was, in some instances at least, followed by fatal results. The great mass of these extracts consisted of fatty acids, and as the chemists could find nothing else present, they very naturally concluded that the fatty acids themselves constituted the poisonous substance.

Since the overthrow of the fatty acid theory, various other conjectures have been given, but none of them are worthy of credit.

We make the following quotations from some of the best recent authorities on the subject to show their opinions:

¹ Ibid, 1828, B. 1, S. 65.

² A Treatise on Poisons. First American from the fourth Edinburgh edition, p 496.

³ Archiv f. physiologische Heilkunde, 1853.

“Nothing definite is known of the nature of cheese poison. Its solubility seems established from an observation of Hussemann—a case in which the poison was transmitted from a nursing mother to her child¹.”

“The older investigations of the chemical nature of cheese-poison, which led to the belief of ‘putrefactive cheese acids’ and other problematic substances are void of all trustworthiness, and the discovery of the active principles of poisonous cheese may not be looked for in the near future, on account of proper animals for controlling the experiments with the extracts, as dogs can eat large quantities of poisonous cheese without its producing any effect.”²

“All kinds of conjectures concerning the nature of this poison have been formed, but all are even devoid of historical interest; because they are not based upon experimental investigations. My own experiments towards solving this question have not progressed very far.”³

Other authorities might be cited but all state substantially the same thing.

History of the Michigan Cases.—In the years 1883 and '84 there were reported to the Michigan State Board of Health, about 300 cases of cheese-poisoning. As a rule the first symptoms appeared within from two to four hours after eating of the cheese. In a few the symptoms were delayed from eight to ten hours and were very slight. The attending physicians reported that the gravity of the symptoms varied with the amount of cheese eaten, but no one who ate of the poisonous cheese wholly escaped.

One physician reported the following symptoms: “Every one who ate of the cheese was taken with vomiting, at first of a thin, watery, later a more consistent reddish colored substance. At the same time the patients suffered from diarrhoea with watery stools. Some complained of pain in the region of the stomach. At first the tongue was white, but later it became red and dry, pulse was feeble and irregu-

¹ Dr. Arnold Hiller, *Die Lehre der Faulniss*. Berlin, 1879, S. 197.

² Hussemann, *Real-Encyclopedia der gesamten Heilkunde*, 1881, B. VI S. 313.

³ Brieger, *Ueber die Ptomaine*, 1885, S. 50.

lar; countenance pale, with marked cyanosis. One small boy, whose condition seemed very critical, was covered all over his body with bluish spots.

Dryness and constrictions of the throat were complained of by all. In a few cases the nausea and diarrhoea were followed by marked nervous prostration.

Notwithstanding the severity of the symptoms in many, there was no fatal termination. Many of the physicians at first diagnosed the cases from the symptoms as due to arsenical poisoning and administered ferric hydrate. Others gave alcohol and other stimulants, and treated upon the expectant plan.

The Poisonous Cheese.—All of these 300 cases were caused by eating of twelve different cheeses. Of these nine were made at one factory and one each at three other factories. Of each of the twelve, I received smaller or larger pieces. Of each of ten, I received only small amounts. Of each of the other two I received about eighteen kilograms. The cheese was in good condition and there was nothing in the taste or odor to excite suspicion. However from a freshly cut surface, there exuded numerous drops of a slightly opalescent fluid which reddened litmus instantly and intensely. (Although as I have stated, I could discern nothing peculiar in the odor, if two samples, one of the good, the other of poisonous cheese, were placed before a dog or cat, the animal would invariably select the good cheese.) But if only poisonous cheese was offered, and the animal was hungry it would partake freely. A cat was kept seven days and furnished only with poisonous cheese and water. It ate freely of the cheese and manifested no untoward symptoms. After the seven days, the animal was etherized and abdominal section was made. Nothing abnormal was discovered. I predicted however in my article on poisonous cheese,¹ that the isolated poison would affect the lower animals. As to the truth of this prediction we will see later.

My friend, Dr. Sternberg, the eminent bacteriologist, found in the opalescent drops, above referred to, numerous micro-

¹ Ein Ptomain aus giftigem Kase. Zeitschrift für physiologische Chemie, B. X, S. 146.

cocci. Inoculation of rabbits with these failed to produce any results.

Extracting the Poison.—At first I made an alcholic extract of the cheese. After the alcohol was evaporated in vacuo at a low temperature, a residue consisting mainly of fatty acids remained. I ate a small bit of this residue and found that it produced dryness of the throat, nausea, vomiting and diarrhoea. For some weeks I endeavored to extract the poison from these fatty acids, but all attempts were unsuccessful. I then made an aqueous extract of the cheese, filtered this and drinking some of it, found that it also was poisonous. But after evaporating the aqueous extract at 100° on the water-bath, this residue was not poisonous. From this I ascertained that the poison was volatile at or below the boiling point of water. I then tried distillation at a low temperature, but by this the poison seemed to be decomposed.

Finally I made the clear, filtered aqueous extract, which was highly acid, slightly alkaline with sodium hydrate, agitated this with ether, removed the ether and allowed it to evaporate spontaneously. The residue was highly poisonous. By re-solution in water and extraction with ether the poison was separated from foreign substances. As the ether took up some water this residue consisted of an aqueous solution of the poison. After this was allowed to stand for some hours in vacuo over sulphuric acid, the poison separated in needle shaped crystals. From some samples the poison crystallized from the first evaporation of the ether and without standing in vacuo. This happened only when the cheese contained comparatively a large amount of the poison. Ordinarily the use of the microscope was necessary to detect the crystalline shape. From sixteen kilograms of one cheese I obtained about 0.5 gram of the poison, and in this case the individual crystals were plainly visible to the unaided eye. From the same amount of another cheese I obtained only about 0.1 gram and the crystals in this case were not so large. I have no idea, however, that by the method used, all of the poison was separated from the cheese.

Properties of the Poison.—I have called this poison tyrotoxicon (cheese poison). It gives with potassium ferricyanide and ferric chloride Prussian blue. It also reduces iodic acid. However, I do not consider either of these reactions characteristic and a number of other substances will also give them. Peptones, a small amount of which is present in all milk, will give these reactions. The ordinary alkaloidal reagents failed to produce any precipitate with tyrotoxicon. The crystals have a penetrating, old-cheesy odor, and it is interesting in this connection to state that Hussemann and Boehm have both observed this odor in poisonous sausage. If the crystals be allowed to stand exposed to the air at ordinary temperature, they decompose with the formation of an organic acid whose nature has not been determined. Tyrotoxicon is soluble in water, alcohol, chloroform and ether. I am sorry that I have not been able to obtain this substance in quantities sufficient for an ultimate analysis. But the smallness of the amounts obtained and the rapid decomposition of the poison has prevented any such analysis.

The physiological test for the poison I regard as the only certain one. A few drops of an aqueous solution of these crystals placed upon the tongue produced the symptoms already described as characteristic of poisonous cheese. This was tried repeatedly upon myself and upon some of my students who kindly offered themselves for experimentation.

THE POISON IN MILK.

In November, 1885, a student brought to me a four ounce bottle partly filled with milk which had stood tightly closed with a glass stopper for about six months. From this I succeeded in isolating the same poison. It was recognized by its crystalline appearance and by its effect upon myself. It was presumed that this milk was normal in composition when first obtained; but of this we could not be certain.

I then put several gallons of normal milk in perfectly clean bottles with glass stoppers and allowed these to stand in my work room. From time to time a bottle was opened and the test for tyrotoxicon was made. These tests were followed by

negative results, until about three months after the experiment was begun. I then succeeded in getting the poison from one of the bottles. The method for testing for it was as follows: The coagulated milk was filtered through heavy Swedish filter paper. The filtrate was colorless and decidedly acid in reaction. It was rendered feebly alkaline by the addition of potassium hydrate, then agitated with ether. After separation the ethereal layer was removed with a pipette, allowed to run through a dry filter paper to remove a flocculent white substance which floated in it, and then allowed to evaporate spontaneously. If necessary this residue was dissolved in water and again extracted with ether. On the evaporation of the ether the tyrotoxin was recognized by its crystalline appearance, by its odor, and by placing a small bit on the tongue. As the ether takes up some water, there is usually enough of the latter left after the spontaneous evaporation of the ether to hold the poison in solution, and in order to obtain the crystals this aqueous solution must be allowed to stand for some hours in vacuo over sulphuric acid.

From one-half gallon of milk there was obtained quite a concentrated aqueous solution of the poison after the spontaneous evaporation of the ether. Ten drops of this solution placed in the mouth of a small dog three weeks old, caused, within a few minutes, frothing at the mouth, retching, the vomiting of frothy fluid, muscular spasm over the abdomen, and after some hours watery stools. The next day the dog seemed to have partially recovered, but was unable to retain any food. This condition continuing for two or three days, the animal was killed with chloroform. No examination of the stomach was made.

It may be remarked here that I have elsewhere pointed out the necessity of using pure ether for these extractions, as some samples of ether contain an irritating, ptomaine-like substance.

POISONOUS ICE-CREAM.

June 13, 1886, I received from Dr. Henry Baker, Secretary of the Michigan State Board of Health, a pint bottle about two-thirds full of melted ice cream, with the request that I

analyze it, as some eighteen persons had been seriously affected by eating of it. Dr. Baker also sent some of the vanilla which had been used as flavoring. It was thought that the poison would be found in the vanilla, because some lemon ice cream furnished at the same gathering had not affected those who ate of it. As the readiest means of deciding this, my assistant Mr. Novie, and myself, took at first thirty drops each of the vanilla extract. No ill effects following this, Mr. Novie took two teaspoonfuls more, with no results. This settled the question of the poisonous nature of the vanilla more satisfactorily than could have been done by a chemical analysis.

We then added distilled water to the cream, and after thorough agitation, filtered it. The filtrate was tested for tyrotoxin by the method already given. The aqueous solution, after the spontaneous evaporation of the ether, was given to a cat. Within ten minutes the cat began to retch, and soon it vomited. This retching and vomiting continued for two hours, during which time the animal was under observation, and the next morning it was observed that it had passed several watery stools. After this, although the cat could walk about the room, it was unable to retain any food. Several times it was observed to lap a little milk, but on doing so it would immediately begin to retch and vomit. Even cold water produced this effect. This condition continuing, after three days the animal was placed under ether and its abdominal organs examined. We certainly expected to find marked inflammation of the stomach. But we really did find the stomach and small intestines filled with a frothy, serous fluid, such as had formed the vomited matter, and the mucous membrane very white and soft. There was not the slightest redness anywhere. The liver and other abdominal organs seemed to be normal.

It should be remarked that this cat was about two months old. Attention is called to this, because young animals are affected by this poison much more readily than older ones. It requires a comparatively large amount of the poison to cause any marked symptoms in an old cat.

After having made these experiments I received from Dr. R. C. Moffit, of Lawton, Mich., the following letter :

"LAWTON, Mich., June 21, 1886.

"DEAR DOCTOR :—I understand from Prof. Charles Lawton, of this place, that the cream sent to Lansing, for examination, has been forwarded to you, so I write to give you the particulars. About two hours after eating the cream every one was taken with severe vomiting, and after from one to six hours later with purging. The vomit was of a soapy character, and the stools watery and frothy. There was some griping of the stomach and abdomen, with severe occipital headache, excruciating backache and 'bone' pains all over, especially marked in the extremities. The vomiting lasted from two to three hours, then gradually subsided, and everybody felt stretchy, and yawned in spite of all resistance. The throats of all were cedematous. One or two were stupefied ; others were cold and experienced some muscular spasms. A numb feeling, with dizziness and momentary loss of consciousness, was complained of by some. Temperature was normal, and pulse from 90 to 120. Tongue, dry and chapped. All were thirsty after the vomiting subsided, and called for cold water, which was allowed in small quantities, with no bad results. After getting out no one of the victims was able to be in the hot sun for several days, and even yet (about ten days after the poisoning) the heat affects myself. I attended twelve persons, besides being sick myself, and all were affected in pretty much the same way. Several complain yet of inability to retain food on the stomach without distressing them. The man who made the cream took a teaspoonful of it, and he vomited the same as those who ate a whole dish, but not so often nor for so long a time. All are affected with an irresistible desire to sleep, which can scarcely be overcome. Even yet, some of us feel that drowsy condition, with occasional occipital headache. Yours fraternally,

"R. C. MOFFITT, M. D."

It will be seen from the above that the symptoms produced in the persons agree closely with those observed in the cat. Cases of poisoning from ice-cream are by no means rare, and I hope that those who have the opportunity will not fail to test for tyrotoxin. In the report of the Brooklyn Board of Health for 1885, an instance is given of the poisoning of more than 100 persons from ice-cream sent out from one restaurant. The chemist was unable to detect any mineral poison. The injurious results were attributed to the use of decomposed gelatin ; but no gelatin of any kind was used in the Lawton cream. Other cases occurring in New York and Brooklyn have been attributed to the employment of artificially prepared

vanilline for flavoring ; but the vanilla extract used in the Lawton cream was not poisonous, as has been shown.

The circumstances under which tyrotoxicon develops require further study. As has been shown above it may develop in normal milk, kept in a clean bottle for three months ; but it is evident that in some instances it appears much earlier. The production of the ptomaine is, in all probability, due either directly or indirectly, to the growth of some micro-organism. In the cheese Dr. Sternberg found a new micrococcus ; but whether or not there is any relation between this organism and the poison remains to be determined. In the cheese, milk, and cream, in all of which I have found the poison, there was present more or less butyric acid, and it may be that there is some intimate relation between butyric acid fermentation and the production of the poison. Some years ago Selmi obtained a ptomaine which resembles coniine, and pointed out that it might be formed by the action of butyric aldehyde on ammonia, thus : $2C_4H_8O + NH_3 - 2H_2O = C_8H_{16}N$. or with butyric acid thus :



In like manner other fatty acids may react with the decomposing nitrogenous substances, forming alkaloidal bodies. Tyrotoxicon has no special resemblance, so far as is known, with coniine, but the possibility of these alkaloidal substances being formed in this way is worthy of mention. T. Lauder Brunton, in referring to the writer's discovery of tyrotoxicon, states that from the action of the substance he would infer the presence of two poisons. This is altogether possible. The writer has not been able to obtain the poison, as yet, in quantities sufficient to enable him to make an ultimate analysis of it. But that it is a chemical body produced by fermentation there can be no doubt.

If there be any doubt about the poison being produced by fermentation, the following experiment would seem to clear it up.

June 26, I took two samples, of one pint each, from a bottle of milk which had already undergone the lactic acid fermentation. These samples were placed in clean glass graduates.

To one, a piece of the solid portion of the poisonous custard, about the size of a filbert, and which had been washed with distilled water, was added. To the other no addition was made. These samples stood side by side for forty-eight hours. Both were then tested for tyrotoxin. The one to which no addition was made gave no crystals, no odor, and when given to a cat produced no effect. The one to which the addition had been made yielded crystals which had the odor of tyrotoxin, and which, when given to a very large old cat, produced frothing at the mouth and retching, but no vomiting or diarrhoea, and the next day the animal was able to eat food and seemed to have recovered. I am quite certain that had this been administered to a young animal the result would have been more marked.

It is well known that milk, while undergoing the lactic acid fermentation, does not possess any such poisonous properties as those belonging to tyrotoxin. There is no evidence, then, that the poison is connected in any way with the ordinary decomposition of milk. The following extracts from a letter just received from the maker of the Lawton cream shows that the attention given to the milk and vessels was all that could be desired :

“The milk of which the cream was made was fresh and sweet morning's milk, only reserving with it the cream of the milk of the night before from the same cows. The milk is kept in a cool, clean milk cellar. The custard was made about noon that day and immediately afterwards the process of freezing was begun. The vessels were all thoroughly cleaned. There was no possibility of any impurities adhering to them, for they were scalded, wiped and dried before being used. The only ingredients used were the milk, cream, eggs, sugar (best granulated) and the flavoring.

“The lemon cream was frozen first, then taken out, put into the packers, and packed solid with ice and salt. Then the vanilla cream was frozen in the same manner. I used the best Jennings's extract, about the usual quantity, not in excess. The cream was eaten in the evening by many people of the village. All of those who ate of the vanilla cream were made sick, and none of those who ate of the lemon cream suffered any inconvenience.

“Now, the milk was the same in both, milked from the same cows the same morning that the cream was made, so that there was no difference in the custard used in making the vanilla cream and the lemon cream, but it turned out that the one made people sick and the other did not.”

“We have continued making cream since in the same manner without the

least change of the ingredients or the apparatus, except we have not used vanilla extract, but lemon and pine-apple, and it has been freely eaten and no one has been made sick by it.

"Clearly in my mind the milk does not account for the trouble. One thing further : of course the cream which you examined has been made since the ninth day of June, and may have undergone changes which would result in generating the poison referred to in the papers [certain newspaper accounts of the finding of the poison], and which would not have been found in the cream had it been examined when fresh.

"If there is anything farther that I can furnish you in regard to facts or circumstances in connection with the ice-cream, I will be willing at any and all times to give the fullest information possible. Hoping to receive the correct analysis soon, I remain yours respectfully.

"J. W. JOHNSON."

That the poison which I found in the cream was the same as that which affected the people can not be doubted after comparing the symptoms produced in the cat with those observed by Dr. Moffitt ; and as has been stated, the experiment on the cat was made before I received the letter from Dr. Moffitt. The cream was made on the 9th of June, and the poison separated on the 14.

I wrote to Mr. Johnson asking several questions, which he has kindly and fully answered. As the nature of the questions is shown in the answers, I will simply give the answers:

"(1.) The milk from all the cows was mixed together in the making of the custard."

"(2.) The custard for the lemon and vanilla was all one custard ; made and mixed before the extracts were put in."

"(3.) We had previously used the same brands of extracts (Jennigs's best), both lemon and vanilla, with no bad results."

"(4.) The food of the cows in the morning and evening consists of oats and corn, ground together and fed dry, with clover hay. I have never seen anything suspicious in the pasture or food. There is a running stream of water, coming from a spring in the pasture. There is plenty of shade. At evening the cows are driven from the pasture and placed in the stable or yard, according to the season. The stable and yard are open for inspection at any time. My residence is in the centre of the village, and the board of health would not

allow me to stable and yard my cows there if there were any bad odors during the summer."

"(5.) The teats are thoroughly washed before each milking."

After receiving the above details concerning the making of the cream, the following experiment was made :

July 8. To one quart of night's milk a piece of the solid portion of the Lawton cream, about the size of a filbert, was added. This residue had been left on the filter paper ever since the analysis of the poisonous cream, June 14, and it was on June 8 when the first milk for the preparation of the Lawton cream was collected. This dried and hardened lump was crumbled into the milk, which was placed in a clean tin pan and set in a cool cellar. July 9, to a quart of morning's milk, another small bit of the infected material was added, and this milk was also placed in the cellar. At 1 P. M. both portions of milk were poured into a clean earthenware jar, and four fresh eggs beaten, and one pint of granulated sugar were added. The whole was thoroughly agitated, then allowed to stand at the temperature of the room until 4 P. M., when it was placed in the ice-box of a refrigerator, surrounded by ice and here kept until 7 A. M., the next morning, July 10. Then three ounces of the custard was stirred up with distilled water, filtered, the filtrate rendered alkaline and agitated with ether. The residue on the evaporation of the ether was dissolved in a little water and given to a kitten about two months old. Immediately the kitten manifested the symptoms of poisoning by tyrotoxin, which have already been described. I began the analysis of this custard in the morning before having my breakfast, and getting a little on my finger in carrying the jar, I tasted of it. Within a very few minutes I was nauseated, and ten minutes after taking it I vomited. The prompt action of so small a quantity was probably due to the condition of my stomach. At 2. P. M. of the same day I took one teaspoonful of the custard. Within thirty minutes there was marked nausea and some violent retching, but no vomiting. At 3 P. M. the symptoms having abated, I took a tablespoonful more of the custard. At about 3.30, I began to vomit freely. The nausea continued for about an hour. After

this there would be passing sensations of sickness. At 8 p. m., while visiting a patient, I was taken very suddenly and sharply with nausea and griping pains in the abdomen. I again vomited and had one watery stool. After this there was no farther trouble. The occipital headache, mentioned by Dr. Moffitt in his letter, was very marked for some hours after taking the custard. It consisted of sharp, lancinating pains which were confined wholly to the occiput. The nausea was peculiar. I cannot say that there was pain in the stomach. A sickening taste would be felt in the mouth and a peculiar, very sickening odor, which I recognized as that of the isolated poison, would intensify the nausea. The throat and mouth seemed filled with a sticky, tenacious mucus. In short, the effects on these parts resembled those which I have experienced from an over-dose of atropia.

I think that this experiment explains the poisonous nature of the vanilla cream. The fermentation going on in the custard, and probably begun in the milk, was arrested in that part flavored with lemon by the freezing which began immediately. But while the lemon cream was being frozen that part of the custard which was to be made into vanilla cream continued to ferment, and before the freezing process was begun enough of the poison was generated to seriously affect those eating of it.

The maker of the cream does not give us any exact information concerning the length of time which elapsed between the making of the custard and the freezing of that portion of it flavored with vanilla. He only states that the lemon cream was frozen first. Recently I have received from Lawton a letter giving me more exact information on this point, also some valuable knowledge concerning the conditions under which the cream stood. I take from this letter the following extract: "The cream was frozen in the back end of an old wooden building on Main street. It is surrounded by shade, has no underpinning and the sills have settled into the ground. There are no eve-troughs and all the water falling from the roof runs under the building, the streets on two sides having been raised since the building of the house. The building had been unoccupied for a number of months, consequently

has had no ventilation, and what is worse, the back end (where the cream was frozen) was last used as a meat market. The cream which was affected was that portion last frozen; consequently it stood in an atmosphere more like that of a privy vault for upwards of an hour and a half or two hours before being frozen. It seems to me that anything so sensitive to surroundings as milk could not escape being affected by such an atmosphere."

The above, from a non-professional, but evidently, a very sensible observer, furnishes information of great value.

It should be remarked that in the custard which I made there was nothing peculiar in the taste. It was sweet and pleasant. But while it was not at all acid to the taste, it gave a decidedly acid reaction as tested by litimus, and was not amphoteric in reaction, as cow's milk frequently is.

It is possible that the presence of the large amount of albumen in the custard, from the eggs, hastened the fermentation. I believe that makers of cheese have found by experience that a large amount of albumen in cheese renders decomposition more easy.

How the special germ which produces the poison found its way into the Lawton cream I cannot say; but that it was either present in the milk or was contained in the eggs used, I think cannot now be doubted.

The discussion of the possible relation between tyrotoxicon and cholera infantum will be omitted here as it would not be suited to a chemical journal.

NOTE.—Since the above article was read at Buffalo tyrotoxicon has been found in milk by Drs. W. K. Newton and Shippen Wallace of New Jersey, (See Philadelphia Medical News, Sept. 25, 1886) and by Prof. Sherver, chemist to the Iowa State Board of Health.

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ON THE MELTING POINT OF FATS.*

BY H. W. WILEY.

The fats pass rather slowly from the semi-solid state, which is their natural condition at ordinary temperatures, to complete fluidity. It is, therefore, difficult to determine accurately the exact temperature at which they melt.

The value of the melting point in the examination of fats is at once apparent, provided it is possible to be assured that it represents a definite temperature which can be easily and accurately determined.

I have been led to a careful consideration of this subject by the investigations which have lately been made under my direction, of the adulterations of butter. The fats which are used as adulterants of butter have certain chemical and physical properties, by which they may be distinguished from it. For example, I mention specific gravity, crystalline structure and melting and solidifying points. If these physical properties can be studied and appreciated as thoroughly and well as the chemical composition of fats, there will be little difficulty in determining whether a given sample is pure butter or an adulterated article.

The differences in specific gravity found in the various fats are very small, and yet every analyst recognizes the value of an accurate determination of this property. For instance, at a temperature of 40° pure butter fat has a specific gravity of .912, while the substitutes therefor, viz: lard, tallow, oleo-oil, neutral lard, etc., have specific gravities varying from .900 to .905. Yet even these small differences are extremely valuable in distinguishing the fats from each other. So too in respect of the crystalline structure of fats it is found that the slight differences that exist, especially with polarized light, afford valuable data for discrimination.

I believe that differences in melting points when they can

* Read at the meeting of the American Association, for the Advancement of Science, Buffalo, Aug. 1886; communicated by the author.

be accurately determined, will prove equally helpful to the analyst. The usual methods employed hertofore have been based on the assumption that a fat becomes transparent at the moment it assumes the liquid state. Usually the fat is melted and placed in glass capillary tubes, and after cooling put into water near the bulb of a thermometer. The water is slowly warmed, and the moment the fat in the tube becomes transparent the reading of the thermometer is taken. A careful observer is able in this way to make multiple determinations which agree well together, but the readings of different persons are apt to vary greatly. Moreover it is not the *melting* but the *transparent* point that is determined.

In 1883, at the Minneapolis meeting of the Association, I described a method of determining the flowing point of a fat. The melted fat having been put into a small, bent metallic tube, was, after cooling, placed in a bath of mercury. One arm of this "U" tube was slightly longer than the other. The bent tube was immersed in the mercury until the longer arm was just below the surface. The fat in the tube was, therefore, subjected to a certain definite pressure from the mercury, due to the difference in length of the two arms. When the melted fat first appeared on the surface of the mercury, the thermometric reading was made. It is scarcely necessary to add that the bulb of the thermometer was wholly immersed in the mercury. Fairly good results were obtained by this method.

Another method which gave rather good results I tried at the same time. A thin film of fat was spread over the surface of the mercury and the temperature noted at which a platinum wire drawn through it left no trace. The solidifying point was determined in the same operation by observing where the wire left a mark. Various methods for determining the melting point of fats are given by Reichardt.¹ The method preferred by the author is a modification of Guichard's process,² in which the fat is forced out of a tube by a water pressure of a constant magnitude.

1. Zeit. Anal. Chem. Vol. 25, pp. 11 et seq.

2. Op. cit. Vol. 22, p. 70.

Dr. H. Krüss³ describes an apparatus for estimating the melting point by the completion of an electric circuit dependent on the melting of the fat used as an insulating material. A platinum wire bent into the form of a small hook is dipped into the melted fat, a portion of which adheres to it. This process is repeated until a sufficient insulation is produced. The fat covered end of the wire is then dipped into a mercury cup which contains also a bulb of the thermometer. The cup is placed in the electric circuit and the moment of contact is determined by the ringing of an electric bell. Thorough trial of this method convinced me that it was less accurate than any of those which have already been mentioned.

Realizing the importance of determining some definite point at which fats would assume a constant condition under the influence of temperature, I was led to select an entirely new physical aspect of fats, easily and certainly visible, which could be regarded as the melting point. This condition may be defined as the point at which the molecular attraction of the fat becomes greater than the molecular cohesion.

If a thin film of any fat be suspended in a liquid of equal specific gravity with it, and this liquid be slowly warmed, a point will be reached at which the film will roll up and finally assume the form of a sphere. By imparting to the globule a gentle motion of rotation the observer is easily able to distinguish the moment when it becomes sensibly symmetrical. I use the following method and apparatus for applying this principle to the determination of the melting point of fats. The apparatus is shown by the accompanying figure. It consists of :—

1. An accurate thermometer for reading easily tenths of a degree.
2. A less accurate thermometer for measuring the temperature of water in the large beaker glass.
3. A tall beaker glass, 35 cm. high and 10 cm. in diameter.

3. Zelt. f. Instrumentenkunde, Vol. 4, pp. 32-33. Jan. 1884.

4. A test-tube, 30 cm. high and 3.5 cm. in diameter.
5. A stand for supporting the apparatus.
6. Some method of stirring the water in the beaker. I use a blowing bulb of rubber and a bent glass tube extending to near the bottom of the beaker, as shown in the figure.
7. A mixture of alcohol and water of the same specific gravity as the fat to be examined.

MANIPULATION.

The discs of the fat are prepared as follows: The melted and filtered fat is allowed to fall from a dropping tube, from a height of 15 to 20 cm. on a smooth piece of ice floating in water. The discs are from one to one-and-a-half cm. in diameter and weigh about 200 milligrams. By pressing the ice under the water the discs are made to float on the surface, whence they are easily removed with a steel spatula.

The mixture of alcohol and water is prepared by boiling water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot the water is poured into the test-tube already described, until it is nearly half full. The tube is then filled with the hot alcohol. It should be poured in gently down the side of the inclined tube to avoid too much mixing. If the tube is not filled until the water has cooled the mixture will contain so many air bubbles as to be unfit for use. These bubbles gather on the disc of fat as the temperature rises and finally force it to the top of the mixture.

The test-tube containing the alcohol and water is placed in a vessel containing cold water and the whole cooled to below 10° . The disc of fat is dropped into the tube from the spatula and at once sinks until it reaches a part of the tube where the density of the alcohol-water is exactly equivalent to its own. Here it remains at rest and free from the action of any force save that inherent in its own molecules.

The delicate thermometer is placed in the test-tube and lowered until the bulb is just above the disc. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disc the thermometer is moved from

time to time in a circularly pendulous manner. A tube prepared in this way will be suitable for use for several days, in fact, until the air bubbles begin to attach themselves to the disc of fat. In no case did the two liquids become so thoroughly mixed as to lose the property of holding the disc at a fixed point even when they were kept for several weeks.

In practice, owing to the absorption of air, I have found it necessary to prepare new solutions every third or fourth day.

The disc having been placed in position, the water in the beaker glass is slowly heated and kept constantly stirred by means of the blowing apparatus already described.

When the temperature of the alcohol-water mixture rises to about six degrees below the melting point, the disc of fat begins to shrivel, and gradually rolls up into an irregular mass.

The thermometer is now lowered until the fat particle is even with the centre of the bulb. The bulb of the thermometer should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotary movement should be given to the thermometer bulb, and I have thought it would be convenient to do this with a kind of clock-work, although I have not carried this idea into execution. The rise of temperature should be so regulated that the last two degrees of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so, the reading of the thermometer is to be made. As soon as the temperature is taken, the test-tube is removed from the bath and placed again in the cooler. A second tube containing alcohol and water is at once placed in the bath. It is not necessary to cool the water in the bath. The test-tube (I use ice water as a cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum about 1.5° above the melting point of the fat under examination.

Working thus with two tubes about three determinations can be made in an hour.

After the test tube has been cooled, the globule of fat is removed with a small spoon attached to a wire before another disc of fat is put in.

AGREEMENT OF MULTIPLE DETERMINATIONS.

Filtered Butter Fat.

No. 1	by one observer	33.5°
No. 2	by another	33.5
No. 3	by a third	33.9
No. 4	“ “	32.4
No. 5	“ “	34.4

A second set of observations made with the same butter gave :

No. 1	33.7°
No. 2	33.8
No. 3	33.5
No. 4	33.5

A different butter gave the following numbers :

No. 1	34.0°
No. 2	33.7
No. 3	33.8
No. 4	34.0

Another butter, “Creamery Tub,” gave the numbers below:

No. 1	33.7°
No. 2	33.7
No. 3	33.6
No. 4	33.6

A neutral lard from Armour & Co., Chicago, gave the following results :

No. 1	42.8°
No. 2	42.4
No. 3	42.3
No. 4	42.6
No. 5	42.2
No. 6	42.0

An oleo-oil from Armour & Co., gave :

No. 1	29.4°
No. 2	29.5
No. 3	29.5
No. 4	29.7
No. 5	30.0
No. 6	30.3
No. 7	29.7
No. 8	29.8

Another butter, shown by the microscope to be adulterated, gave :

No. 1	33.5°
No. 2	33.7
No. 3	33.5

No. 1777, a doubtful butter gave :

No. 1	34.3°
No. 2	34.5
No. 3	33.6
No. 4	34.0

No. 1779, also a doubtful butter gave :

No. 1	34.2°
No. 2	33.5
No. 3	33.0

These results show that the method is capable of general application, and will give multiple results which agree far better than those obtained by any other method heretofore in use.

Collecting together the mean results obtained with butter fats, the following table is obtained :

TABLE NO. I.

<i>Serial No.</i>	<i>Melting Point.</i>	<i>Sol. Acid.</i>	<i>Sp.Gr. at 40°.</i>
1745	34.5°	5.48	.911
1766	34.3	4.52	.910
1768	34.2	5.21	.910
1769	33.7	5.05	.912
1772	34.0	5.26	.911
1785	32.0	4.48	.912
1786	34.7	4.32	.912
Mean	33.8	4.86	.911

TABLE NO. II.

Melting points, etc., of butters of doubtful purity :

<i>Serial No.</i>	<i>Melting Point.</i>	<i>Sol. Acid.</i>	<i>Sp. Gr. at 40°.</i>
1777	34.1°	3.92	.910
1779	33.6	3.16	.909
1780	34.4	3.02	.910
1781	34.5	3.97	.910
Mean	34.1	3.51	.909

The above were all bought as pure butters. They are condemned on account of the low percentage of soluble acid, while by their specific gravity, they appear to fall within the limit of purity. The soluble acid in the above was determined by washing out, and not by Reichert's method.

TABLE NO. III.

Melting point of substances sold as butter but proved by analysis to be adulterated :

<i>Serial No.</i>	<i>Melting Point.</i>	<i>Sol. Acid.</i>	<i>Sp. Gr. at 40°.</i>
1755	39.0°	1.53	.906
1778	33.6	0.21	.904
1787	34.6	0.09	.906
4594	35.4	0.09	.904
4594	37.8	0.00	.905

TABLE NO. IV.

Melting point, etc., of "oleo-oil" and "Neutral lard" used as butter adulterants :

NEUTRAL LARD.

<i>Serial No.</i>	<i>Melting Point.</i>	<i>Sol. Acid.</i>	<i>Sp. Gr. at 40°.</i>
1754	42.4°	0.10	.904
4597	42.4		

"OLEO-OIL."

1756	29.7°	0.08	.903
4596	29.6	0.08	.903

TABLE NO. V.

Melting point of mixtures made in laboratory as indicated. The butter used had a melting point of 33.1°; the "oleo-oil" of 29.6°; and the "neutral lard" of 42.4°.

<i>No.</i>	<i>Composition of Mixture.</i>	<i>Theoretical Melting Point.</i>	<i>Observed Melting Point.</i>
1.	2 parts butter, 1 part "neutral"	36.2°	35.2°
2.	1 part butter, 2 parts "neutral"	39.3	39.6
3.	1 part butter, 1 part "neutral" and 1 part "oleo"	35.0	35.5
4.	2 parts butter, 1 part "oleo"	31.9	32.0
5.	1 part butter, 2 parts "oleo"	30.8	30.5

From the above it appears that the melting point of a mixture of two or more fats can be readily and accurately calculated from that of its constituents. The agreement, except in No. 1, is within the error of ordinary observation.

REMARKS ON PRECEDING DATA.

The mean melting point of the butters examined is 33.8°. The maximum is 34.7° and the minimum 32.0°. In one case, however, a butter known to be genuine showed a melting point of 37.7; but this unique result was so widely different from any other that I did not include it in the table. This butter was made in the laboratory from a small quantity of sweet cream. In general terms it may be said that a genuine butter will show a melting point falling within the limits of 33° and 34°.

Of butter adulterants the "neutral lard" has a comparatively high melting point and "oleo-oil" a low one. Unfortunately for analytical purposes, it is easy for the fabricator to make an artificial butter whose melting point is sensibly the same as that of the genuine article. On the other hand it is seen that if a false butter be made of a genuine one and only one of the adulterants in common use, the variation of the melting point from the normal will be sufficiently great to call attention to the falsification.

EFFECT OF TIME ON MELTING POINT OF THE FAT DISCS.

By some variations in the melting point of fat discs of different ages my attention was directed to an investigation of the effect of time.

The following data will serve to measure the influence of age on the melting point:

BUTTERS.

No.	Melting Point directly disc was made.		Melting Point.	Increase or Decrease.
1.	33.1°	after 24 hours	33.6°	+0.5°
2.	34.3	" " "	34.7	+0.4
3.	34.2	" " "	34.6	+0.4
4.	34.5	" " "	35.2	+0.7
5.	32.9	" " "	32.8	-0.1
6.	33.1	" " "	34.5	+1.4

In every case, except No. 5 in the above table, it is seen that the melting point of the discs of butter was raised by standing on water at ordinary temperatures for 24 hours.

In one instance a butter whose melting point was 34.5° stood in the form of discs from May 27 until August 3. An attempt was made on this latter date to determine its melting point. At a temperature of 75° the disc had not assumed a spherical shape and the temperature could be carried no higher on account of approaching the boiling point of the alcohol.

ADULTERATED BUTTERS.

No.	Melting Point directly disc was made.		Melting Point.	Increase or Decrease.
1.	34.6°	after 5 days	61.4°	26.8°
2.	32.9	after 18 hours	37.0	4.1
3.	38.1	" 24 "	42.9	5.9
4.	35.3	" 46 "	35.3	0.0
5.	37.8	" 44 "	40.3	2.5

Again in every case but one a marked rise in the melting point.

"OLEO."

Oleo at once	29.6°
Oleo after 42 hours	32.5
<hr/>	
Increase	2.9

It would appear from the above results that adulterated butters and butter adulterants show a greater rise in melting points when the discs are a day or more old than pure butter. The analytical data, however, are too meagre to permit a definite statement of this kind. Should it prove to be true, it

would be a valuable indication in the discrimination between pure and adulterated butters. An examination of the old discs with the microscope did not reveal a crystalline structure, and this change, therefore, must be attributed to a molecular modification or superficial oxidation.

EFFECT OF THE PRELIMINARY HEATING OF THE FAT TO DIFFERENT TEMPERATURES.

A butter fat was melted at a low temperature and allowed to stand until the temperature had fallen to 30° . It was still perfectly fluid. The discs were formed by dropping on ice as usual. The melting point obtained was 33° . The fat was now heated to 50° and treated as above. Melting point, 33.4° . The temperature was raised to 80° . Melting point, 32.8° . The above results, falling within the possible error of observation, show that the temperature to which the fat is subjected before the formation of the discs has no appreciable effect on the point at which the fat particle becomes a sphere.

EFFECT OF A SUDDEN RISE OF TEMPERATURE.

A sudden rise of temperature tends to greatly lower the melting point. A fat which showed a melting point of 35.3° when determined in the usual way melted at once into a perfect sphere when dropped into the water-alcohol mixture having a temperature of 29° . At 28.5° the globule was irregular.

A disc of neutral lard, having by the usual method a melting point of 42.4° , became at once a sphere when dropped into the water-alcohol at 36.2° . Below that temperature the spheroidal shape was not symmetrical.

In all cases this phenomenon will appear. It may be suggested, therefore, with strict propriety, whether this may not be regarded as the proper melting point. Since the temperature at which the spheroidal state is assumed can be determined within one or two degrees by a preliminary trial, it would not be difficult to have a series of mixtures of water and alcohol arranged so as to show differences of temperature at 0.5° . By dropping the discs successively into these mix-

tures the instantaneous fusing point could be determined with accuracy.

GENERAL CONCLUSIONS.

The method set forth in the preceding paper has been proved by 165 determinations to be capable of giving agreeing results. Not only will the numbers obtained by the same observer be concordant but also those of different analysts. This arises from the fact that the moment of the assumption of the spheroidal state is easily determined even by an unpractised eye. I have also noticed that in this condition pure butter and "oleo" are quite transparent, while on the other hand neutral lard and adulterated butters are still somewhat opalescent. From this it is seen that the data obtained by the old method of determining the temperature of transparency would differ somewhat from those obtained by the proposed procedure. Since the age of the disc has a great deal to do with its melting point, I suggest that all determinations be made within 15 minutes to 2 hours from the making of the discs.

The method can also be extended to such bodies as paraffine and beeswax. The melting point of a paraffine was found to be.

No. 1	55.6°
No. 2	55.1
No. 3	55.2
No. 4	55.3

An interesting phenomenon was observed in determining the melting point of the paraffine which may be made to show in a lecture experiment the change of volume which bodies sometimes undergo in passing from a solid to a liquid state. The same mixture of water and alcohol used in the examination of fats, allowed the disc of paraffine to sink to about the same point as the discs of fat. When the temperature rose, however, to within one or two degrees of the melting point, there was a sudden increase in volume. The pellet of paraffine rapidly rose to the top of the tube. To avoid this and keep the globule within the liquid, I made a mixture of water-alcohol and absolute alcohol. With this arrangement the rise

of the paraffine was arrested in the upper third of the tube where its assumption of the spheroidal state could be readily observed. On placing the tube in a cooling bath the globule of paraffine rapidly sinks as it solidifies. The discs of paraffine and beeswax are quite irregular, but nevertheless suitable for the process. The melting point of the one sample of beeswax examined was found to be 64.2° .

COMPOSITION OF STROMEYERITE.*

BY GEORGE A. KOENIG, PH. D.

STROMEYERITE has been identified from Zacatecas, Mexico. At this locality the miners designate the various silver minerals by their colors, as black silver, red silver, green silver and blue silver. Under the latter name—*plata azul*—several minerals are undoubtedly comprehended, but probably the most prevalent is the mineral here identified as Stromeyerite. One large specimen is composed of numerous prismatic crystals, the terminations broken off—resting on well-crystallized quartz, and from several smaller specimens it would appear that quartz is the ordinary associate of Stromeyerite at Zacatecas, while the other silver minerals—Proustite, Polybasite, Stephanite, Argentite—are more commonly associated with calcite. The faces of the crystals are rough, not admitting accurate measurements; the prismatic angle is near 120° – 119° . The mineral has no cleavage. Its fracture is uneven to flat subchondoidal and very splintery. The lustre is brilliantly metallic and the color iron-gray with a strong bluish purple admixture. The color of the powder is nearly the same. It is not sectile, but mild, and has a hardness of 3.5.

Spec. gravity=6.2303, made upon 1.623 grams of fragments from several crystals. Before the blowpipe it melts very readily to a globule, emitting sulphur dioxide, and changing to a gray globule of silver-copper. Gives no sublimate on charcoal, nor in open or closed tube, and dissolves in nitric acid, giving a blue solution, in which hydrochloric acid precipitates flocculent silver chloride.

A preliminary analysis made with a fragment from one crystal (0.2346 grm.) gave the result I; a second analysis made upon the mixed fragments used in the determination of specific gravity (0.5 gr.) gave the result II.

* Read before the Acad. Natl. Sci., Phila., June 29, 1886; communicated by the author.

- I. $\text{AgCl} = 0.1615$; $\text{Cu}_2\text{S} = 0.0958$; $\text{BaSO}_4 = 0.2837$.
 II. $\text{AgCl} = 0.2509$; $\text{Cu}_2\text{S} = 0.2105$; $\text{BaSO}_4 = 0.5758$.

From this we calculate :

	I.	II.
Insoluble	—	0.26
Ag	51.66	50.18
Cu	32.67	33.69
S	16.64	15.81
	<hr/>	<hr/>
	100.97	99.94

Analysis II having been made with twice the quantity of substance and with greater care, deserves alone to be taken as basis for the atomic ratio. Dividing the percentages by the atomic weights, we obtain :

$$\text{Ag} : \text{Cu} : \text{S} = 0.4661 : 0.9983 : 0.4975.$$

$$\text{Ag} + \text{Cu} : \text{S} = 0.5322 : 0.4975$$

$$= 2.007 : 1$$

Hence, $47\text{Ag}_2\text{S} + 53\text{Cu}_2\text{S}$.

It is seen that Ag and Cu are not exactly in the ratio 1 : 1, but very near. Undoubted Stromeyerite has been described heretofore only from two localities, Schlaugenberg, in Siberia, and Rudelstadt, in Silesia, and from the latter place only, in crystals. The analyses of the mineral from these places do not give the ratio of 1 : 1 for Ag and Cu either, but a little closer than the present locality of Zacatecas. Since Ag_2S and Cu_2S may replace each other isomorphically in all proportions without question, we may look upon such a ratio as Stromeyerite demands, 1 : 1, as quite an exception, owing, no doubt to peculiar conditions present at the time of crystallization.

The material for this investigation was obtained from Dr. A. E. Foote, who collected it during his recent visit to Zacatecas and other mineral localities in Mexico.

A NEW METHOD FOR DISTINGUISHING BETWEEN ANIMAL AND VEGETABLE FIBERS.

BY DR. HANS MOLISCH.

FOR a long time chemists have sought to find a method for determining rapidly whether a fiber is of vegetable or animal origin.—the odor of the fiber on burning and its appearance when carbonized and incinerated; its behavior towards solution of caustic potash of a certain strength; towards nitric acid; ammoniacal solution of copper, towards a mixture of sulphuric and concentrated nitric acid, etc., have been used as distinguishing tests.

The chemist knows that these tests tried singly give no certain result, and that several of the reactions must be tried before even arriving at a half conclusion. None the less he gladly uses them since the use of a microscope is often inconvenient. In contrast to the expert microscopist who is able to distinguish by a single glance through his microscope, the chemist must often fall back upon these reactions. This circumstance as well as the incompleteness of the chemical tests already known prompted me to make known two new methods for distinguishing between vegetable and animal fibers, which in certainty and convenience surpass all those heretofore known.

My process is founded upon two new sugar reactions which I discovered during the year and described in full. (Compare *Sitzungsberichte der k. Akademie der Wissenschaften zu Wien*, May, 1886, Bd. 93. Abtheilung II.) As I have shown there, the sugars (cane sugar, grape sugar, maltose, milk sugar and fruit sugar), give with alpha naphthol and thymol very characteristic reactions. If, for example, 5 c. c. of a sugar solution is mixed with two drops of a 15–20 per cent. alcoholic solution of alpha naphthol and then concentrated sulphuric acid added in excess, a beautiful deep violet coloration ensues on shaking the mixture. If the mixture is then diluted with water a bluish violet precipitate forms after some time.

If, instead of alpha naphthol thymol is used in the same way a cinnabar-ruby-carmine-red, flocculent precipitate is formed. The delicacy of this sugar test is very extraordinary, and as I have satisfied myself, greater than that of the Trommer and Fehling tests. This is shown best by the remarkable fact that normal human urine, which certainly contains only a very small amount of sugar, gives this reaction even when diluted with water 100–300 times.

The same reactions are also given *indirectly* by the carbohydrates and glucosides, since by treating these with sulphuric acid, according to circumstances, either immediately or after a short time, sugar is formed. As the cellwalls of plants consist largely of a carbohydrate, cellulose, this may be detected, even if the metamorphosis has gone very far, as in the case of cork or wood.

By mixing the cellulose with water and sulphuric acid, the cellulose is changed into sugar, and this is the reason that *plant fibers* (cotton, linen, hemp, jute &c.) give indirectly the sugar reaction. *Animal fibers* contain neither sugar nor carbohydrates; they do not therefore, give the reaction with alpha naphthol or thymol. In this way we are placed in a position to decide, by means of a simple and convenient reaction, upon the origin of any fiber.

After many experiments the following process has proved to be the best. To about .01 gm. of the well boiled and washed fiber 1 c. c. water is added in a test-tube, then two drops of an alcoholic 15–20 per cent. alpha naphthol (beta naphthol does not give the reaction) solution, and finally, concentrated sulphuric acid (a bulk about equal to the volume of liquid). If the fiber is of vegetable origin the whole liquid by shaking takes a deep violet color and the fiber dissolves. If, on the contrary it is of animal origin the liquid becomes yellow to reddish brown in color.

If thymol is used instead of the violet color a beautiful cinnabar-carmine-red is obtained, especially if diluted with water.

I have obtained satisfactory results with a great variety of plant fibers—cotton, linen, hemp, jute, sunn, china grass,

ramie, phormium, aloe, musa, cocoa, pissave and straw fiber, &c.

Since cell walls in which cellulose can only be found indirectly, as wood, cork and the fungi, give the same reaction, we can conclude that every plant-membrane gives the above alpha naphthol and thymol reactions. On the contrary animal fibers (as sheeps wool, mohair, alpaca and vicuna wool, camels-hair, &c.) give no reaction since they contain neither sugar nor any substance which forms sugar when acted on by sulphuric acid.

Silk behaves like hair and wool, except that many sorts both true silk and the so-called "wild silk" give a very weak transient reaction especially if they have been boiled for a long time. These samples evidently contained traces of a substance which is changed into sugar by the sulphuric acid. Sugar is not present for if it were the silk which had been boiled with water would not give the reaction.

The coloration is, however, so slight and continues so short a time that one is never in doubt whether it is caused by the silk or by a plant fiber. On account of the great delicacy of the test it is necessary when wool is tested that a clean material should be used, free from the so-called "wool lice" and burdocks. These being of vegetable origin would give the reaction and lead to erroneous results. In the process as above given, fiber which has been boiled is specified. The reason for this is that in finishing many fabrics, especially silk goods, gum, flax seed mucilage or sugar is used to brighten the luster. The boiling and washing of the fiber is to remove these substances which would give the reaction.

From what has been said it might be supposed that these reactions would only be applicable to uncolored fibers and not to dyed fiber, but this is not the case. The color which is obtained from colored animal fibers in carrying out the alpha naphthol test is usually not a violet, and when it approaches this color it is easily distinguished from that produced by sugar or vegetable fibers by its weakness and by fading after a short time. The coloring matter neither obscures the reaction nor hinders it from taking place. It is

therefore, for our purpose, immaterial whether the fibers are colored or not. By using the alpha naphthol test and at the same time noticing the solubility or insolubility of the fiber we can determine whether a fabric is purely vegetable or animal, or of a mixture of both, or of silk only.

Fabrics which do not give the alpha naphthol sugar test or only weak- ly and transiently.	}	Dissolves completely,	Silk.
		Does not dissolve	Wool.
		Dissolves partly	Wool and Silk.

Fabrics which give the tests beautifully.	}	Dissolves completely	{ Plant fiber or fiber mixed with silk.
		Dissolves partly	{ Plant fiber and wool and possibly also silk.

If, not the goods in the piece, but the warp and wood separately, are tested, still closer conclusions can be drawn and in many cases all the different fibers in a fabric may be determined.—*Dingler's Polytechnisches Journal*, 261, 135.

ABSTRACTS.

APPARATUS AND REAGENTS.

An Apparatus for Washing and Drying Precipitates with exclusion of the carbon dioxide of the air is described by Ad. Jolles (*Zeit. f. anal. chemie* **25**, 369). The cylinder, fig. 1, has

a ground top and upon this a ground glass plate is placed. The plate is well greased so as to make an air tight joint. In the plate there are three openings through which pass three perforated rubber corks. The figure shows the further arrangement of the apparatus. The substance in solution is poured into the cylinder, the cover fitted on and the precipitant added through *a*. The precipitate is allowed to deposit and the supernatant liquid decanted by means of the siphon. While the liq-

Figure 1.

uid is running out through the siphon, air passes through the small bottle containing caustic potassa, which deprives it entirely of its carbon dioxide. Fresh water is then added through the funnel tube and the washing continued in the same way as before. After the washing is completed the precipitates

produced may be dried by fastening a clay cylinder to the end of the siphon tube by a rubber tube; the other end of the siphon is inserted in a cork placed tightly in one opening of a Woulf's bottle. The other neck of the bottle is connected with a filter pump, and after about $1\frac{1}{2}$ hours the precipitate collects on the clay cylinder as a compact mass which is easily transferred to a desiccator and dried.

Two New Forms of Combustion Furnace have been described by Julius Schober (*Zeit. anal. Chem.* 25, 365). In the first form the tube is supported in a clay trough made in short sections. This trough is supported by means of side flanges resting on a recess in the bricks which form the sides of the upper part of the furnace. The flanges are perforated to allow the flame to pass through. The side bricks are placed in a perpendicular position and are supported by lugs cast on them which pass over an iron bar. The cover is made of arched, perforated bricks laid on over the trough and upon the upper edge of the side-bricks. See figure 2. The furnace is also provided with a new arrangement for raising and lowering the burners. This consists of a flat rod placed below the tube carrying the burners and which has wedge shaped pieces fastened to its upper surface. Corresponding wedge shaped pieces are fastened to the lower side of the tube carrying the burners. On drawing out the rod the burners are raised. The tube carrying the burners is kept in position by a rod which is fastened to it at right angles and passes through a slot in a plate fixed to the base of the furnace.

Fig. 2.

The second form of furnace is shown in figure 3.

By means of the screw a system of burners can be raised and lowered at will. The upper rods against which the bricks rest are fastened to moveable arms *e*, which can be held together by means of the clamp *f*. The tube rests upon bridges *g*, of which as many may be used as are necessary. The upper

Figure 3

edges of the bricks have grooves cut in them to allow the passage of the hot gases from the furnace. Both forms of furnace are said to be efficient and convenient.

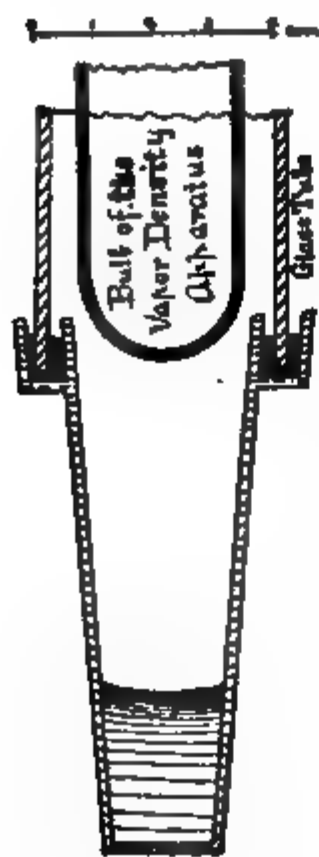
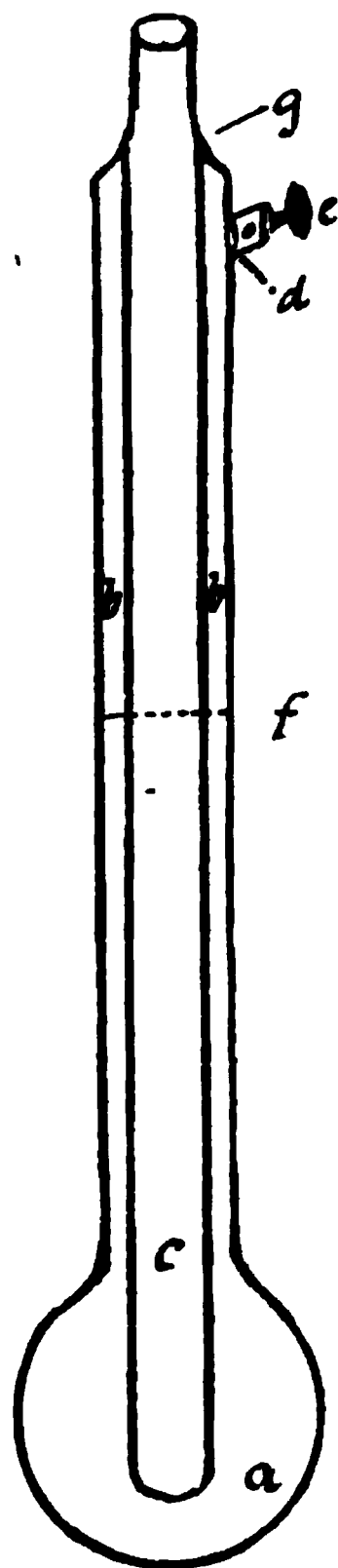


Figure 4.

Determination of Vapor Density.—Victor Meyer, Ber. d. deut. Chem. Ges. 19, 1861. The glass tube used for heating the material which is to form the bath may be replaced by the apparatus shown in figure 4. The lower vessel is made of cast iron and is connected by a mercury lute with the glass cylinder. This arrangement is intended for heating naphthalene, thymol, &c.,—substances boiling from 100° – 300° . For substances boiling above 300° , a vessel made entirely of iron is necessary. The advantages of this arrangement are that the glass cylinder seldom breaks and if it does do so it can be replaced easily and cheaply.

A New Apparatus for Melting Point Determinations.—

C. F. Roth, *Berichte d. deut. chem. Gesellschaft*, 19, 1970. In giving melting points no correction is commonly made. This would make less difference if the determination were always made in the same way but this is not the case. Sometimes the thermometer is dipped in sulphuric acid and some-



times the determination is made according to Anschütz's method—the thermometer being enclosed in a kind of air bath. This difficulty is remedied by the apparatus shown in figure 5. The apparatus has the following dimensions: diameter of *a* 65 mm. Total length of flask, 200 mm. Diameter of neck of flask 28 mm. Diameter of tube *c* 15 mm. The tubulure *d* is 11 mm wide and is closed with a hollow stopper *e* with a side opening. The flask is filled with colorless sulphuric acid to *f*. The stopper is then turned so that the openings in *d* and *e* correspond, and the heat applied below, the thermometer being suspended in the inner tube. Experiment proves that there is a difference in temperature between the upper and lower part of this air bath of 3–4 degrees when the heat is slowly raised which causes an error of .16°, which is however of small importance and may be disregarded. The author has compared the melting points of six substances taken in the ordinary way in sulphuric acid and with his apparatus and finds the results almost identical. The only objection to the apparatus is, that it is difficult to reach tem-

Fig. 5. peratives higher than 250°.

Thermometer for Lecture Experiments. — F. C. G. Müller, *Berichte d. deut. chemischen Gesellschaft*, 19, 2175. The need of a thermometer which can be read at a distance of say 8 m. has been met in the following manner. The liquid used is concentrated sulphuric acid blackened by the

addition of a little sugar. This liquid expands uniformly, and has $3\frac{1}{2}$ times the coefficient of expansion of mercury. The thermometer is made in the ordinary form, the scale being drawn on a strip of card. The scale just below and above 0° , 100° and 200° is colored carmine-red, and above and below 50° and 150° , green. The author prepared such a thermometer six years since which he is still using. The cost of such a thermometer should not exceed 4 marks (\$1). Comparison with a new thermometer gave the following results :

Hg	-20.6°	0	40.5	100	205.
H ₂ SO ₄	-21°	0	40.5	99.5	204.

Preparation of Pure Sulphuretted Hydrogen.—Otto Freiherrn von der Pfordten, Ann. d. Chemie, **234**, 262. Oxygen is removed by passing the gas through a solution of chromous chloride. In order that the gas may be free from hydrogen and arseniuretted hydrogen, it is prepared from calcium or barium sulphide and hydrochloric acid. To remove vapors of hydrochloric acid the gas is led through a solution of potassium sulphide or over lumps of the solid sulphide. If the presence of a little CO₂ in the gas does no harm, potassium carbonate can be used instead. To dry the gas it is led over phosphorous pentoxide, sulphuric acid will not answer as it decomposes the gas with separation of sulphur. As phosphorous pentoxide contains phosphorous it is necessary to free the sulphuretted hydrogen from oxygen before passing it over this material, as otherwise, the gas is decomposed and sulphur separates.

Hydrogen Free From Oxygen.—Von der Pfordten, Ann. d. Chem., **234**, 567. According to the author's experiments, hydrogen made from zinc and acid contains no oxygen. This statement made in a former paper (Ibid. **228**, 124) is confirmed by the behavior of titanium sulphide, which is very sensitive to oxygen, when heated in this gas.

The Preservation of Gases over Mercury.—H. B. Dixon, in a paper read before the British Association and published

in the Chemical News, (54, 227) discusses the question, can gases be preserved for any considerable time over dry mercury. The author answers this question in the affirmative, provided the gas is collected over hot, pure mercury, so as to exclude any film of moisture or impurity. In the discussion which followed the reading of the paper, Mr. Crookes and Sir H. Roscoe gave it as their opinion that the purity of the mercury was the essential condition for preventing diffusion, which depended on the formation of a film between the mercury and the glass.

The Use of Phosphorous Pentoxide.—Joh. Walter, Jour. f. prak. Chem., 34, 133. The great bulk of phosphorous pentoxide stands in the way of its application as a reagent. To remedy this a rubber cap with an opening in the centre is drawn over the bottle in which it is kept. Through this opening a large glass rod is passed and the pentoxide compressed into a cake. Cylinders are then cut from the cake by means of a cork borer.

Preparation of Litmus Paper.—Bornträger, Zeit. f. anal. Chem., 25, 333, prepares a very sensitive paper by acidifying a watery extract of litmus with sulphuric acid until decidedly acid and then adding caustic soda until a strip of paper dipped in the solution and dried shows the proper color. Proper paper for this purpose is hard to find, but the filter paper, No. 597 of Schleicher & Schüll, has been found to answer the purpose very well.

For Standardizing Normal Alkalies and Acids.—Bornträger, Zeit. anal. Chemie, 25, 233, has found potassium bitartrate a very excellent material, as it is scarcely at all hygroscopic and can easily be obtained perfectly pure. For standardizing acids, the bitartrate is calcined, the acid added in slight excess and the excess determined with normal alkali. The bitartrate is prepared as follows: cream of tartar is heated with 1 part of water and $\frac{1}{10}$ part of hydrochloric acid, sp. gr. 1.13 for several hours. The crystals of bitartrate obtained on cooling are washed with cold water repeatedly, dissolved in hot water,

recrystallized and dried. It is considered pure when a given weight, titrated against normal alkali and the same weight, calcined and titrated against normal acid, require equal volumes of the normal solutions. Bitartrate prepared in this way gave by direct titration with alkali, 79.84 per cent. tartaric acid; by titration with alkali after calcining 79.80 per cent.—Theory 79.79 per cent.

Phosphorous Tetroxide.—T. E. Thorpe and A. E. Tutton, Jour. Chem. Soc., 49, 833. A small quantity of the mixed oxides, obtained by the slow burning of phosphorous in air dried by means of phosphorous pentoxide and oil of vitriol, was transferred to a tube previously filled with dry carbon dioxide, the carbon dioxide exhausted and the tube sealed. On heating the oxides in the tube to 290° a considerable quantity of red suboxide formed, and a sublimate of clear, transparent and highly lustrous crystals was obtained. These crystals belong to the orthorhombic system and have a composition corresponding to the formula P_2O_4 . When dissolved in water, phosphorous and orthophosphoric acids are formed. It is possible that this oxide is isomorphous with antimony tetroxide, as cervantite, the native form of antimony tetroxide, is also orthorhombic.

A Reliable Method for Cracking Glass Tubes.—E. Beckmann, Zeit. f. anal. Chem. 25, 531. A mark is made on the tube with a file at the point where the tube is to be broken. On each side of this mark, strips of wet filter paper are wrapped around the tube, each strip several layers in depth, so as to leave a space 2 mm. wide between them. By the application of a small blowpipe flame to this part of the tube the crack can be carried around it without deviating from a straight line. Beakers, flasks, watch-glasses, funnels, etc., can be cracked in the same way.

INORGANIC ANALYSIS.

Iodine in Blowpiping.—H. A. Wheeler and C. Ludeking, Trans. St. Louis Acad. Science, IV, 676.* The authors prepare supports for blowpipe use by pouring a cream of plaster of paris upon a lightly greased glass plate (only a little oil should be used lest the plate turn black by its charring). The reagent consists of an iodide of sulphur, obtained by fusing together 40 parts iodine with 60 parts sulphur. When the metals or their compounds are heated with this reagent on the plaster tablets sublimates are obtained which coat the plates. It is necessary to use the oxidizing flame to avoid deposition of soot.

COLOR OF THE IODIDE COATS.

Arsenic—A reddish-orange.

Lead—A chrome-yellow.

Tin—A brownish-yellow.

Silver—A bright yellow while hot; faint grayish-yellow when cold; is close to the assay.

Antimony—An orange red.

Mercury—Scarlet and yellow, the yellow changing completely to scarlet on standing.

Selenium—A reddish-brown.

Tellurium—A purplish-brown.

Bismuth—A chocolate-brown fringed with red near the assay.

Cobalt—A greenish-brown edged with green; the brown color is evanescent, changing into faint green, especially when breathed upon.

Molybdenum—A deep ultramarine; is close to the assay, and is the permanent oxide Mo_2O_6 .

Wolfram—A faint greenish-blue; is a permanent oxide, Wo_2O_6 ; is close to the assay, and is brought out stronger by dropping on more acid [HI] after the operation.

* From a reprint sent by the authors.

Copper—White.

Cadmium—White.

Zinc—White; is very volatile.

“As the copper, cadmium and zinc iodides are white, the tablet should first be coated with a film of soot by holding it in a smoky flame, in order to give a black background to show off these white coats.

These three white coats closely resemble one another in their properties, and in order to distinguish them it is necessary to blow on them vapors of ammonium sulphide, when they are converted into their sulphides, and consequently will turn black in the case of copper, yellow with cadmium, and remain white with zinc. The copper iodide also gives the characteristic blueish-green color to the flame as it passes off, so that it can be readily determined even in the presence of zinc and cadmium.

If to the peculiar velvety-appearing chocolate-brown coating of bismuth a drop of dilute ammonia be added, or ammonia vapors be blown over it, the brown disappears, leaving a brilliant red coat.

Many of these coats are more or less evanescent, and disappear on prolonged exposure at ordinary temperature.

These coats will be found to be very striking and characteristic, and are very delicate, when compared with the usual blowpipe tests. It will be further observed that we are now able to distinguish tin and zinc in the presence of each other, which has hitherto been impossible with the blowpipe alone.

In the case of complicated mixtures, the above metals cannot be satisfactorily distinguished from one another by this reagent, and it will not answer as a substitute for the old method, that necessitates a separation of them into groups. But for individual cases and confirmatory tests, especially when delicacy is required, it will be found to be a most valuable acquisition to the blowpipe outfit.”

The paper is accompanied with three lithographic plates showing the sublimates as above given.

Detection of Calcium in the Presence of Strontium.—C. L. Bloxam, Chem. News, 54, 16. The strontium is precipitated by means of sulphuric acid, and to the filtrate ammonia and arsenic acid are added. The calcium is thrown down in the form of crystalline, ammonium calcium arsenate, the crystals agreeing in appearance with the salt $\text{Ca NH}_4 \text{AsO}_4 \cdot 7\text{H}_2\text{O}$ described by Wach. The small quantity of strontium left in solution does not precipitate. The precipitate is very insoluble. "A solution containing Ca in 113,235 of water which gave a distinct crystalline precipitate almost immediately with ammonia and ammonium oxalate, also gave one, after a minute or two, with ammonia and arsenic acid, and the precipitate was far more crystalline than the oxalate. The corresponding magnesium salt is quite different in appearance under the magnifying glass. Commercial pure strontium nitrate and carbonate were found to contain much calcium.

The Determination of Calcium as Ammonia-Arsenate.—C. L. Bloxam, Chem. News, 54, 170. When ammonia in slight excess is added to a solution of calcium containing arsenic acid a white precipitate of $\text{Ca NH}_4 \text{AsO}_4 \cdot 7\text{H}_2\text{O}$ is formed. Over sulphuric acid in a vacuum this changes to $\text{Ca}_3\text{NH}_4\text{H}_2(\text{AsO}_4)_6 \cdot 3\text{H}_2\text{O}$. Dried at 100° the salt becomes $\text{Ca}_3\text{NH}_4\text{H}_2(\text{AsO}_4)_6 \cdot 3\text{H}_2\text{O}$, containing theoretically 20.85 per cent. Ca. Found 20.00 and 19.66 per cent. Ca. When ignited it has the composition $\text{Ca}_2\text{As}_2\text{O}_7$ but becomes slightly alkaline and loses a little arsenic.

The author proposes to make use of this precipitate as a means of estimating calcium; the advantages being that the precipitate filters much more rapidly, and, when dried at 100° , contains only 20 per cent. Ca. The disadvantages are that it must be washed with ammonia water and that it must be dried at 100° . The author's own test analyses show that the method is far less exact and it is difficult to see that the process possesses any real advantage. If magnesium is present this is also thrown down as $\text{MgNH}_4\text{AsO}_4$ and this certainly cannot be called an advantage.

Detection and Estimation of Iodine Bromine and Chloride.



—M. Dechan, Jour. Chem. Soc. **49**, 68. For qualitative determinations the operation is carried out in the following way: Solution of potassium dichromate ($40\text{K}_2\text{Cr}_2\text{O}_7$ to 100 H_2O) is added to the substance to be examined and the mixture boiled, the distillate being caught in a test-tube containing water and a drop of CS_2 . If iodine is found the boiling is continued until the vapors no longer turn starch paste blue. If the boiling is long continued water must be added to the solution, the volume of which must not fall below $\frac{2}{3}$ of that originally taken. Then for every 100 c. c. of dichromate solution 8 c. c. dilute H_2SO_4 is added (1 acid to 1 water) and the liquid boiled, the vapors being tested for bromine with CS_2 as before. After all the bromine is driven off the liquid in the flask is tested for chlorine in the ordinary way with silver nitrate.

For quantitative work, the operation is carried out in the same manner—4 gms. substance and 100 c. c. potassium dichromate solution being used. The distillate of iodine is received in a solution of potassium iodide and titrated with 1% thiosulphate. The bromine is caught in potassium iodide and estimated in the same way. Finally the chlorine is estimated in the residue with silver nitrate. The test analyses are 3 in number and good as far as they go, except that the chlorine was determined in but one instance. Nothing is said about the behavior of the insoluble haloid salts.

Note on J. Lawrence Smith's Method for the Estimation of Alkalies and Silicates.—Philip Holland, Chem. News, **54**, 242. Mr. Holland has examined Smith's method with a view to two points, first to ascertain whether it is necessary to fuse again the residue left after the first fusion and extraction with water, and second, whether any serious loss is caused by volatilization of the chlorides during the heating.

With reference to the first question, 1 gm. of the silicate gave on being again fused an amount of alkali as chloride which varied in weight from .0029 to .0040 gms.

As to the second point, .2362 gms. $\text{KCl} + \text{NaCl}$ after fusing with calcium carbonate and ammonium chloride in the ordi-

nary way for 40 minutes left .2345 gms. $\text{KCl} + \text{NaCl}$. In a second experiment .3173 gms. mixed chlorides gave .3152 gms.

Determination of Nitric Acid.—Morse & Linn Amer. Chem. Jour. 8, 274. The method is a modification of the Tiemann-Schulze process. The nitric acid is converted into nitric oxide by ferrous chloride in an atmosphere of carbon dioxide, and the nitric oxide absorbed by a solution of permanganate. 3 solutions are needed.

1. A solution of potassium permanganate of such strength that 1 c. c. = .015 gms. KNO_3 according to the reaction $\text{KMnO}_4 + \text{NO} = \text{KNO}_3 + \text{MnO}_2$. This solution is used to absorb the nitric oxide. The strength need not be exactly known.

2. A solution of oxalic acid slightly stronger than 1, i. e., a solution of which 1 c. c. will decompose rather more than 1 c. c. of 1, according to the reaction. $2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 + 5\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 18\text{H}_2\text{O} + 10\text{CO}_2$. The exact strength of this solution need not be known.

3. A dilute, carefully standardized solution of potassium permanganate. [This may as well be made $\frac{N}{10}$].

The apparatus used consists of *a*, a generator for the CO_2 , *b*, a flask containing the substance to be examined; *c*, a tube to condense the vapor of HCl ; *d*, a potash bulb containing a concentrated solution of potassium carbonate to arrest any acid vapor, and *e*, the two absorption tubes. The pieces are connected by rubber tubing and there are clamps between *a* and *b*, *c* and *d*, *d* and *e*. The flask is arranged like the one ordinarily used in the Tiemann-Schulze method.

To make a determination 100 c. c. of solution 1 is placed in the absorbing tubes and a little zinc sulphate added. This seems to facilitate the absorption. The absorption tubes are 2 in number, made of ordinary combustion tubing 650–700 mm. long. They are placed in an inclined position so as to decrease the pressure. The nitrate is then placed in the flask and the apparatus filled with carbon dioxide. The ferric chloride solution is then introduced in the ordinary way and the nitric oxide formed driven over into the absorbing tubes by the

current of carbon dioxide. The contents of the absorbing tubes are emptied into a beaker, 100 c. c. of solution 2, and a little sulphuric acid are then added. Some of the mixed solution is poured back into the absorbing tubes to dissolve the MnO_2 , which separates. The excess of oxalic acid used is then estimated with solution 3. [Let us call the no of c. c. of this used= n .]

Now 100 c. c. of 1 is measured out, 100 c. c. of 2 added, and the excess of oxalic acid determined with 3. [Let us call the no of c. c. used= o].

As the action of the nitric oxide on the permanganate is expressed by the following reaction: $6\text{KMnO}_4 + 10\text{NO} = 3\text{K}_2\text{O} + 6\text{MnO} + 5\text{N}_2\text{O}_5$; [then if the permanganate is % $n-o \times .0021 = \text{gms. HNO}_3$].

Instead of oxalic acid manganous sulphate may be used, the excess being estimated by Volhard's method. The method though slightly more convenient is less exact. 9 test analyses were made in which the maximum difference between the c. c. permanganate required by theory, and that actually used was .05 c. c.

The authors made the CO_2 required to carry out the process from concentrated sulphuric acid and a strong solution of acid sodium carbonate containing undissolved lumps of the same substance. Obtained in this way it is free from air.

Estimation of Caustic and Carbonated Alkali in the same sample of Carbonate.—H. J. Phillips Chem. News, 54, 28. The usual method involves two separate determinations of Na_2O in order to obtain the ratio of Na_2O present as hydrate to that present as carbonate. This may be estimated with fair accuracy in one sample. The method depends upon the fact that recently precipitated BaCO_3 requires as much normal acid to dissolve it as it would take to neutralize its equivalent of Na_2CO_3 . One gm. (or more if the percentages are low) of the sample is taken and dissolved in a flask with 150 c. c. of recently boiled distilled water, a clear solution of BaCl_2 is added in quantity just sufficient to completely precipitate all the combined CO_3 . It is then heated to incipient ebullition and

allowed to cool, phenolphthalein added, and then normal HCl until the color is destroyed. Then an excess of normal HCl is added until the BaCO_3 is dissolved and the excess determined with normal Na_2CO_3 . The normal acid at first added is a measure of the hydrate, and that added to dissolve the BaCO_3 is a measure of the carbonate. Sulphuric acid is inadmissible in the titration unless the theoretical amount of BaCl_2 was used. In the commercial lyes, sulphates being present, the whole of the precipitates produced by the BaCl_2 will not dissolve; but the BaCO_3 not being so fine as the BaSO_4 it is easy to determine when the former has disappeared. No test analyses are given.

In a communication to the same journal, (Ib. 54, 67) W. Upward states that by titrating in the above way he obtained from a certain sample 91.96 per cent. total alkali. By pouring off the liquid before titrating 90.85 per cent. and by filtering first, 88.68 per cent. alkali. These figures make it evident that to obtain concordant results the titrations must always be made in the same manner. He prefers the following method: 20 gms of the white caustic is dissolved in water and BaCl_2 added and diluted with hot H_2O to about a liter in a stoppered bottle. After settling perfectly, the clear liquid is syphoned off and the bottle refilled with hot water. After a second siphoning the precipitate is filtered and washed until free from alkali which does not take long. The ppt. and filter are then treated with normal nitric acid in excess, in a beaker, and the excess determined with standard soda. Duplicates agree to within .05 per cent.

The Volumetric Test for Manganese.—In 1879 (Jour. Chem. Soc. 35, 365.) John Pattison described a method for estimating manganese volumetrically as follows. The manganese was precipitated from a hot solution containing a ferric or zinc salt or both, by means of calcium carbonate and calcium hypochlorite. By this process the manganese is all thrown down as MnO_2 . The precipitate is then digested with a known amount, in excess, of standard ferrous sulphate solution con-

taining free sulphuric acid, and the excess of ferrous salt determined by Penny's method with $K_2Cr_2O_7$.

This process has been examined by R. W. Atkinson (Jour. Soc. Chem. Ind. V. 365) who reports close agreement in duplicates, but that the results are uniformly too low.

Mr. Pattinson in reply (Ibid. V. 422), points out that it is necessary to have zinc present in order to prevent the formation of permanganate, and indicates other sources of error. He states that seven years of experience with the method has confirmed his belief in its accuracy.

Atkinson (Ibid. V. 467) admits that zinc chloride was not used in his determinations, and states that some experiments which he has since made indicate that there is great difficulty in washing out the bleaching powder solution when zinc is present. He promises to further examine the method and report.

Volumetric Determination of Sulphates without Standard Solutions.—H. Quantin, (Comptes Rendus, 103, 402; Monit. Scientif., Quesneville, 1886, 1222; Chem. News, 54, 233.) If, to a hydrochloric acid solution of barium chromate a solution containing sulphates is added, barium sulphate precipitates, and an equivalent amount of chromic acid is set free and remains in solution. If ammonia is now added in excess the barium chromate remaining in solution will precipitate, leaving in solution ammonium chromate equivalent in amount to the sulphate added. If, therefore, we add to equal volumes of the solution of barium chromate, on the one hand pure potassium sulphate in known quantity, and on the other hand a solution containing sulphates, and denote by p and x the quantities of sulphuric acid taken, it is clear that p and x will be proportional to the weight of chromic acid remaining in solution in either case. Hence it results that if we neutralize with ammonia and then bring the two solutions to the same volume equal fractions of the filtrates will contain quantities of chromic acid proportional to the sulphuric acid precipitated. If sulphuric acid is added to equal volumes of these filtrates, and the amount of ferrous solution needed to

reduce each is determined, then the amounts used, n and n_2 ,

will be proportional to p and x that is, $\frac{p}{x} = \frac{n_1}{n_2}$ or $x = p \frac{n_2}{n_1}$, which

becomes on correction $x = p \frac{n_2 - n}{n_1 - n}$.

The solution of barium chromate is prepared as follows : One equivalent of K_2CrO_4 is dissolved in water, 100 c. c. pure hydrochloric acid added, and the solution diluted to a liter. A second solution is made by dissolving one equivalent of $BaCl_2 \cdot 2H_2O$ in water and diluting to a liter; the two solutions are then mixed and filtered, if necessary, to separate barium sulphate which forms if the $BaCrO_4$ contains sulphuric acid, as is often the case. The solution should have the following properties: If neutralized with ammonia, the filtrate must give no precipitate on adding potassium sulphate; if 100 c. c. of the solution is precipitated with ammonia, the whole made up to a liter and 100 c. c. of the clear liquid taken, not more than 0.2 to 0.5 c. c. of the iron solution should be required to reduce the slight excess of chromic acid which it contains.

The solution of ferrous sulphate should be of such strength that $n_1 - n$ and $n_2 - n = 25$ to 35 c. c. The analysis is conducted as follows: Into a liter flask 4 gms. pure potassium sulphate is introduced and then 500–600 c. c. water; when dissolved, 100 c. c. of the chromate solution is added and the flask shaken for 10 minutes, ammonia is now added until the liquid turns yellow and the solution is made up to a liter. After filtering, 100 c. c. of the solution is acidified with 10 c. c. concentrated sulphuric acid, and the ferrous sulphate solution added until a drop gives a light blue tint with potassium ferricyanide solution on a greased plate. The sulphate to be analyzed is then treated in exactly the same way. The first determination gives n_1 the second n_2 , n is then found by taking 100 c. c. of the barium chromate solution and treating as above without any addition of sulphate. If the substance in which sulphuric acid is to be estimated contains metallic

oxides which react with ferricyanide, or acids which precipitate barium, some preliminary treatment is necessary, as follows: 8. gms. of the substance is dissolved in a little hot water, ammonia in slight excess is then added, and the metallic oxides redissolved in nitric acid containing ferric nitrate. The solution is again precipitated by ammonia, adding a little sodium carbonate (excess of which must be carefully avoided), and the liquid is evaporated to dryness; at about 300° all the oxides proper, such as iron and alumina, along with silica and phosphoric acid, are rendered insoluble; the organic matters, if any, are destroyed, and the presence of sodium carbonate prevents the sulphuric acid of the ammonium sulphate from disappearing if the evaporation to dryness has been carried beyond 300° . The insoluble portion is then treated with boiling water and the whole introduced into a 250 c. c. flask and filled to the mark. The solution is filtered and 125 c. c. taken for analysis, that is, 4 gms. of the original substance. If the volume occupied by the insoluble substance is worth notice it may be taken into account within 0.2 c. c. by collecting it on a filter without washing, and determining its volume after drying. This determination can easily be made to within 0.2 c. c. by putting the precipitate in a 50 c. c. flask and filling to the mark with water from a burette.

The author says that by this method results to within .5 per cent. can always be obtained.

[Experiments upon this process made in this laboratory have indicated as a possible source of error the difficulty of keeping the solution of constant strength. When made up as above directed a considerable part of the barium chromate was deposited. If too much hydrochloric acid is added the smell of chlorine becomes noticeable. When made up so as to be .%, adding $2\frac{1}{2}$ times as much acid as above directed, a considerable amount of BaCrO_4 deposited in 24 hours. The solution was then allowed to stand at a rather low temperature (but far above the freezing point) when a noticeable deposit of white crystals, probably barium chloride, was noticed. This formation of crystals is still going on.]

Analysis of Silicates in Connection with Blowpipe Determinations.—W. M. Hutchings, Chem. News, **54**, 173. About .050 to .075 gms of very finely pulverized mineral is placed in the platinum spoon and covered with about 7 or 8 times the weight of ammonium fluoride and the mixture heated gently over a spirit lamp. The fluoride melts in its water of crystallization and then evaporates, carrying with it the silica. When dryness is nearly reached care is taken not to heat it too strongly so as to fuse the fluorides, which should remain as a crust easily shaken from the spoon. This crust is ground in the agate mortar with 4–5 times the weight of the mineral in sodium carbonate, made into a paste with distilled water and fused to beads on platinum wire at a high temperature. The beads are then broken in a steel mortar, ground finely in the agate mortar, and the powder dissolved in water. This treatment avoids the tedious evaporation to dryness of the silica with hydrochloric after fusion.

The Production and Measurement of Gold and Other Minute Metallic Spheres to Determine their Weight.—G. A. Gozdorf Chem. News, **54**, 231. “In making assays for gold where the amount of gold is very small, a little silver is required in which the gold may be collected. As nearly all commercial litharge contains silver, it is rarely necessary to add any for this purpose. Having obtained a prill in which the amount of gold is a third or less than the silver, the prill is boiled in dilute nitric acid in a porcelain capsule to dissolve the silver, and where the amount of gold is more than one dwt. to the ton a second boiling in strong nitric acid should be given. If care is taken in using dilute acid at first, and boiling gently, the gold will be left in one piece of a nearly black color. The acid is now decanted off and the gold washed two or three times in distilled water. The gold may be now placed on an aluminum or other polished metal plate by inverting the capsule and leading the last drop of water and the gold with a glass rod on to the plate; the water is drawn off by a piece of filter paper and the plate gently heated till dry.

Having thus obtained the gold in a pure state, a bead is

made of boracic acid on a platinum wire loop and pressed on the gold while still red-hot; the gold adheres without difficulty, and by heating the bead before the blowpipe the gold is obtained as an almost perfect sphere.

Should the resulting sphere of gold be very minute it is better to measure it under the microscope while in the bead, but if large enough to be seen with the naked eye, it can be measured more accurately after dissolving the boracic acid bead in a watch glass with hot water and placing the sphere of gold on a glass slide.

No other flux seems to possess advantages equal to those of boracic acid for obtaining a sphere of gold. Borax and other fluxes are so fluid when hot that gold is very liable to alloy with the platinum wire.

The following rules and figures may be useful to any one wishing to adopt the system here described:

1. The weight of a sphere increases as the cube of the diameter.

2. The weight of a sphere of any substance of which the specific gravity is known is obtained by multiplying the weight of a unit sphere of water by the specific gravity of the substance and the cube of the diameter.

CONSTANTS FOR USE WITH GRAMME WEIGHTS.

1. Weight of a sphere of water 0.01 mm. in diameter = 0.000,000,000, 523,6 of a gm.

2. Weight of a sphere of gold 0.01 mm. in diameter = 0.000,000,010,210,2 of a gm.

3. Weight of a sphere of gold 0.0x mm. in diameter = $x^3 \times 0.000,000,010,210,2$ of a gm.

4. If 20 gms. of ore are taken for assay the number of grains of gold per ton is found by $x^3 \times 0.008,004$, in which x = the diameter of the sphere of gold in hundredths of a millimeter.

Spheres of silver may be obtained and measured in a similar manner. The boracic acid acts slightly on the silver, but the quantity dissolved is inappreciable, as the action is not

prolonged. The sp. gr. of silver being 10.53, the weight of 0.01 mm. would be $=0.000,000,005,513,518$ of a gm.

Copper, lead, and other metals cannot be melted in boracic acid on platinum wire without dissolving to a perceptible amount, but may with care be melted in sodium carbonate, and, by dissolving the latter in hot water, the sphere of copper, lead, etc., obtained and measured."

Apparatus for Kjeldahl's Method of Nitrogen Determination.—H. P. Armsby and F. G. Short, Amer. Chem. Jour., 8, 323. A flask *a* holding about a liter is closed by a rubber stopper with openings for three tubes. The tube *b* is for emptying the flask, which is effected by connecting with a filter-pump. The exit tube of *c* is inclined slightly upward and connects with the block tin tube of a condenser; *d* is a funnel tube for filling the flask. The annular space around the stem of the funnel tube is filled with glass beads to arrest any particles of alkali.

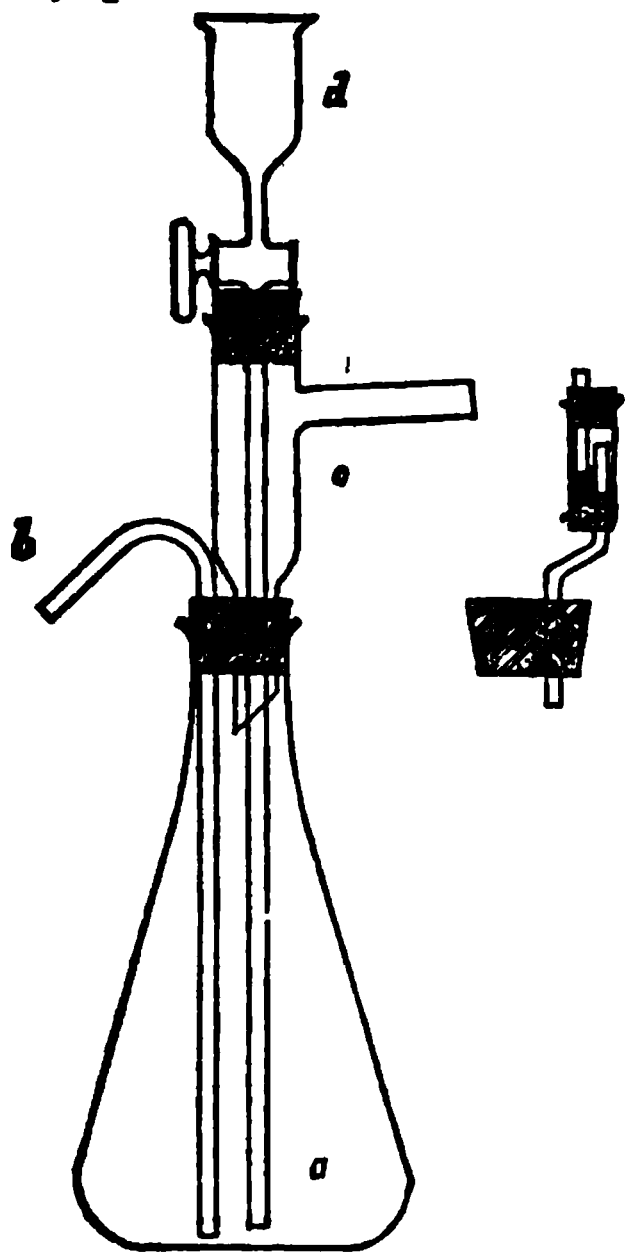


Fig. 6.

In order to prevent regurgitation of the standard acid, a bent tube connected with a mercury trap, as shown in the figure on the right, is fastened in the third hole in the cork. During the distillation the tube *b* is closed by means of a pinch-cock. As used by the authors six flasks and condensers are placed side by side. The condensers are firmly fastened to a light wooden frame, and the water enters at one side and passes through all the condensers successively. The flasks stand upon wire gauze stretched upon two horizontal iron rods about 12 cm. apart, and are sufficiently steadied above by the connection with the condenser. The apparatus is placed upon a small table mounted on casters, and, by simply disconnecting the water and gas, can be wheeled to one side when not in use.

Azotometry and Azotometers.—W. Knop, *Zeit. f. anal. Chem.* **25**, 301. This article is a review of the uses to which the method, introduced by the author, has been put, and of the modifications which he has applied to the apparatus used. In its present form the apparatus preferred may be described as follows : It consists of a large glass jar provided with a tubulure near the base. A metal ring is fastened to the rim of the jar and to this two supports are fastened through which pass rods. These rods reach to the bottom of the jar and can be fastened at any height by means of a screw. One of them serves as a support for the generating bottle and the other for the U tube in which the nitrogen is measured. The generating vessel consists of a wide-mouthed bottle in which is placed the tube containing the urine or other substance to be examined. The glass stopper of this bottle is prolonged into a pipette-shaped vessel having a stop cock on the upper end. This prolongation is filled with glass pearls and serves as a wash bottle for the nitrogen. The upper end of this wash bottle is connected by means of a rubber tube with the upper, graduated end of one arm of the U tube. The other arm of the U tube is open at the top and has an opening near the bottom to which is attached by a rubber tube a glass tube provided with a stop-cock, which passes through a cork fitted into the tubulure in the glass jar. The arms of the U tube are connected below by means of rubber tube so as to make them more flexible.

To operate the apparatus the U tube is filled with water to the 0 mark and placed in the jar filled with water. The substance in which the nitrogen is to be estimated is placed in the tube in the bottle; some of the hypobromite solution is then poured into the bulb containing the glass pearls and the rest into the bottle. The stopper is then inserted and after allowing a few minutes to elapse, so that the excess of hypobromite can drain into the bottle; this is inclined gradually so that the two liquids mix. After complete decomposition has taken place the bottle attached to its support is pushed below the surface of the water, and, after bringing the water in the two arms of the U tube to the same level by means of the

stop-cock which passes through the tubulure of the jar, the volume of nitrogen is read off. The author uses a solution of ammonium chloride as a standard, and, before each determination, the amount of nitrogen given off by the measured volume of this solution is determined and the result gives the correction to be applied in the subsequent analysis. The solution consists of 10 gms. NH_4Cl in 2089.4 c. c. water, and is kept in bottles holding 200 c. c. each. Each c. c. of this solution contains 1 c. c. nitrogen gas measured at 0° and 760 mm.

Microchemical Separation of the Haloid Salts of Silver. — A. P. Smith, *The Analyst*, 11, 126. The haloid salt is treated with strong ammonia and the solution allowed to evaporate on a glass slide, moistened with water, covered with thin glass and viewed with a quarter-inch objective. Ammonio-chloride of silver crystallizes in perfectly formed octahedra, with a maximum diameter of .002 inch, appearing, owing to refraction, more or less opaque, except in the center of the crystal, where the faces are normal to the visual plane. The rate of evaporation has no effect upon the shape, but only upon the size of the crystals. Addition of water to the solution or rapid evaporation gives smaller crystals but does not affect their shape. Ammonio-bromide of silver crystallizes in thin plates of varying size, which appear green, red, and yellow by transmitted light, but are not affected by the polarizer. The solution should not be too concentrated or the greater part of the salt will be deposited in irregularly-shaped prisms. There is no difficulty whatever in discriminating between the chloride and the bromide.

Iodide of silver is amorphous, the size of the granules being about .00005 inch. Chemical tests should, however, be always used to confirm its presence.

Volumetric Estimation of Fluorine. — F. Oettel, *Zeit. anal. Chem.*, 25, 505. The method is founded upon the conversion of the fluorine into silicon tetrafluoride and the measurement of this gas over mercury as in Scheibler's carbonic acid method. The measuring tube consists of a grad-

uated tube contracted at the top and drawn out again cup-fashion. The delivery tube of the flask is ground carefully into this narrow part of the tube; when in use a little mercury is poured into the cup around the joint and acts as a luteing. The measuring tube is drawn out below and connected by a thick rubber tube with another tube, which can be raised and lowered so as to bring the mercury to the same height in both. The passage of the mercury from one tube into the other is regulated by a pinch-cock placed upon the rubber tube. The graduated tube holds 100 to 150 c. c.; a mark *a* is made just below the narrow upper end of the burette, and about 10 c. c. below this the 0 mark of the graduation is placed and the graduation carried on down the tube.

The flask for decomposing the fluoride holds 100 c. c., with a neck 8–10 mm. wide, terminating in a cup-shaped opening into which a stopper is carefully ground; in use a little mercury is poured into this cup around the stopper. The flask has a side neck delivery tube which is bent at an angle of 120° ; the end of the delivery tube is ground into the upper end of the measuring tube as above stated.

To make the analysis the measuring tube is filled to the 0 mark with mercury by raising and lowering the tube, the clamp on the rubber tube is closed, and then concentrated sulphuric acid poured in up to the mark *a*. The substance in which fluorine is to be estimated is then finely ground, mixed with 20 times as much ignited and very finely ground quartz sand, and introduced into the flask, which is then connected with the measuring tube and allowed to stand for 15 minutes to attain the temperature of the air. The thermometer and barometer are read, and 50 c. c. concentrated sulphuric acid is then poured into the flask, (the flask should not be more than half full) the stopper inserted and the mercury poured into the cup shaped opening. By lowering the mercury tube and opening the pinch-cock a decrease of pressure is produced in the flask, which is then heated gently until, in 20–25 minutes, the boiling point of sulphuric acid is reached. The fluorine forms SiF_4 and passes over into the measuring tube; as the mercury sinks in this tube the acid above it wets the sides and absorbs any moisture that may be present.

The apparatus is now allowed to stand for about 2 hours to bring it to the temperature of the room ; the mercury is then brought to the same height in both tubes and the volume of gas, height of the column of sulphuric acid, thermometer and barometer read off. In correcting for pressure 1 cm. sulphuric acid is reckoned to equal 1.359 mm. mercury. The volume of gas is then reduced to 0° and 760 mm.

To estimate the fluorine in fluorides which are easily decomposed by sulphuric acid, the fluoride mixed with quartz is enclosed in a capsule made as follows : potassium bisulphate is fused and one end of a glass tube is inserted and withdrawn ; a drop of bisulphate adheres to the tube and closes it on cooling. The substance is then introduced and the other end of the tube closed in the same manner. When the capsule is dropped into sulphuric acid it remains intact until the acid is heated when the bisulphate dissolves and acid enters the tube. The sulphuric acid used must be concentrated and free from oxides of nitrogen. This can be effected by taking ordinary oil of vitriol and heating it in an evaporating dish with flowers of sulphur until it fumes strongly, then pouring it off from the melted sulphur and boiling down to $\frac{2}{3}$ of its original volume. The heating with sulphur destroys the oxides of nitrogen and the evaporation drives off the water.

TEST ANALYSES.

(1.) Taken 0.4461 gms. CaF_2 . Found 62.13 c. c., calculated 63.25 c. c. SiF_4 ; difference 1.12 c. c. $\text{SiF}_4 = .0038$ gms. $\text{F} = .0078$ gms. CaF_2 . CaF_2 found = 98.25 per cent.

(2.) Taken 0.4823 gms. CaF_2 . Found 66.96, calculated 68.58 c. c. SiF_4 ; difference 1.42 c. c. $\text{SiF}_4 = .0048$ gms. $\text{F} = .0098$ gms. CaF_2 . CaF_2 found = 97.96 per cent.

(3.) Taken 0.2155 gms. CaF_2 . Found 29.20, calculated 30.55 c. c. SiF_4 ; difference 1.35 c. c. $\text{SiF}_4 = .0046$ gms. $\text{F} = .0094$ gms. CaF_2 . CaF_2 found = 95.62 per cent.

(4.) Taken 0.5749 gms. CaF_2 . Found 79.85, calculated 81.51 c. c. SiF_4 ; difference 1.66 c. c. $\text{SiF}_4 = .0113$ gms. CaF_2 . CaF_2 found = 98.03 per cent.

(5.) Taken 0.5710 gms. CaF_2 . Found 79.39, calculated 80.96 c. c. SiF_4 ; difference 1.57 c. c. $\text{SiF}_4 = .0054$ gms. $\text{F} = .0111$ gms. CaF_2 . CaF_2 found = 98.06 per cent.

The author thinks the deficiency in the amount found is due to the absorption of some of the silicon tetrafluoride by the sulphuric acid. He proposes to add 1.4 c. c. SiF_4 to the volume found in each case. The above results would then become :

FLUORINE.

	Found.	Calculated.	Found.	Calculated.
I.	.2183 gms.	.2173 gms.	48.93 per ct.	} 48.72 per ct.
II.	.2349 "	.2350 "	48.70 "	
III.	.1051 "	.1050 "	48.79 "	
IV.	.2792 "	.2801 "	48.56 "	
V.	.2776 "	.2782 "	48.62 "	

[In view of Mackintosh's experiments (see page 10), it is perhaps more probable that the deficiency is caused by hydrofluoric acid which remains dissolved in the sulphuric acid without attacking the silica. Soluble glass, or finely powdered glass or furnace cinder, would probably be a better material than the quartz. One difficulty with the apparatus described above is, that it would be easy to break and difficult and costly to repair.]

The Action of Soda, Lime and Magnesia on ammonium chloride, ammonium magnesium phosphate, ammonium magnesium, chloride, and the two crystallized ammonium zinc chlorides has been examined by Berthelot and Andre (Comptes Rendus, 103, 184). They find that boiling for an hour with soda solution is sufficient to decompose any of these compounds and drive off all the ammonia. When these salts are boiled with milk of lime the ammonia is all driven off, except with the phosphate of ammonium and magnesium which is not completely decomposed even after long boiling. In one case, after boiling for an hour, 2.56 per cent. nitrogen, in another instance 4.95 per cent., was obtained, instead of 7.6 per cent. actually present. Magnesia effects the decomposition much less easily and completely, and perfect decomposi-

tion was not obtained in a single instance with any of the above salts after long boiling.

They obtained the following results :

ACTION OF MAGNESIA ON AMMONIUM SALTS.

SALT.	CONTAINS PER CT. N	BOILED ¼ HR.	BOILED 1 HR.	BOILED 1 ¼ HR.
Ammonium Magnesium Phosphate. . . .	7.6			
(a) " " " "			None.	
(b) " " " "			1.01	
Ammonium Chloride.	26.16			
(a) " " " "		22.85	23.17	23.60
(b) " " " "		23.92	23.92	
(c) " " " "		24.30	24.47	
(d) " " " "		23.72	24.21	
(e) " " " "		22.28	22.82	
(f) " " " "		24.51		
Ammonium Magnesium Chloride. (4NH ₄ Cl+5MgCl ₂ +33H ₂ O)	4.36			
a) " " " "		3.09	3.09	3.09
(b) " " " "		2.76	2.76	2.76
Ammonium Zinc Chloride (ZnCl ₂ +2NH ₄ Cl+½ H ₂ O)	11.00			
		9.39	9.39	9.39
Ammonium Zinc Chloride. (ZnCl ₂ +3NH ₄ Cl+H ₂ O)	13.35	11.52	11.52	11.52

To this Schloësing (Comptes Rendus, 103, 227) replies that magnesia has been constantly used for many years in the estimation of ammonia, and that Boussingault stated long since that lime would not completely decompose ammonium magnesium phosphate *unless the salt was first dissolved*. If the operation is carried out in this way, complete decomposition ensues even with magnesia. Chloride of calcium and still more chloride of magnesium retard the evolution of ammonia, but even when they are present in considerable quantity (27.5 gms. Mg Cl₂) boiling for an hour and a quarter with magnesia effects complete decomposition. He obtains the following results :

Ammonium Chloride, Boiled 40-45 Minutes.

(1) Ammonia found02291 gms.	Theory .02292 gms.
(2) " " " "02301 "	" " "
(3) " " " "06866 "	" .06875 "
(4) " " " "02296 "	" .02292 "

*Ammonium Chloride and Magnesium Chloride (27.5 gms.),
Boiled (1) 75 Minutes, (2) 1 Hour.*

(1)	Ammonia found02282 gms.	Theory .02292 gms.
(2)	" "00222 "	" .002292 "

*Ammonium Chloride + 91 gms. Calcium Chloride, Boiled 55
Minutes.*

(1)	Ammonia found02304 gms.	Theory .02292 gms.
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Ammonium Magnesium Phosphate, dissolved in HCl.

Ammonia found by distillation with lime . .	6.818 per cent.
" " " " magnesia	6.817 "
" actually present	6.936 "

In a subsequent communication (Comptes Rendus 103, 301)
Schloesing gives the following additional results :

Ammonium Magnesium Sulphate, 25 gms. to a Liter.

Ammonia found	{ with potassa .04738 gms.
	{ with magnesia .04746 gms.

Ammonium Zinc Sulphate, 30 gms. to a Liter.

Ammonia found	{ with potassa and sodium sulphide	.05064 gms.
	{ with magnesia .05066 gms.	

Ammonium Copper Sulphate, 25 gms. to a Liter.

Ammonia found	{ with potassa and sodium sulphide	.04396 gms.
	{ with magnesia .04386 gms.	

Ammonium Zinc Chloride, 25 gms. to a Liter.

Ammonia found	{ with potassa and sulphur .08319 gms.
	{ with potassa alone .08306 gms.
	{ with magnesia .08326 gms.

Ammonium Magnesium Chloride, 30 gms. to a Liter.

Ammonia found	{ with potassa .05929 gms.
	{ with magnesia .05936 gms.

The subject is discussed further by Berthelot and Andre,
in another communication. (See Comptes Rendus, 103, 299.)

Separation of Antimony and Tin.—Ad. Carnot, Comptes Rendus, 103,258, has applied the method previously used for the separation of zinc and cadmium (Comptes Rendus, March 15 and 22, 1886) to the separation of antimony and tin. The method is founded upon the simultaneous use of oxalic acid and sodium thiosulphate.

With dilute solutions of tin and antimony in hydrochloric acid, in which the acid is present only in slight excess, oxalic acid gives a white crystalline precipitate of oxalate. In presence of ammonium salts, soluble double oxalates are formed; these double oxalates crystallize only from concentrated solutions and may be diluted largely with water without becoming turbid. From such a solution antimony is precipitated by sulphuretted hydrogen as orange sulphide; stannous salts give a black precipitate, and stannic salts are only incompletely thrown down, especially if the solution is hot and contains a considerable excess of oxalic acid.

Sodium thiosulphate precipitates from such a solution containing tin, on boiling, only sulphur. From the antimony solution sodium thiosulphate throws down a precipitate at first yellow, then orange, vermilion, and, finally, cinnabar red, consisting of antimony oxysulphide. $2 \text{SbCl}_3 + 3 \text{Na}_2\text{S}_2\text{O}_3 = \text{Sb}_2\text{OS}_2 + 6 \text{NaCl} + 4 \text{SO}_2$. On the basis of these observations the following method for the separation of these two metals has been devised:

To the hydrochloric acid solution of antimony and tin ammonia, or ammonium chloride, is added, then about 2 gms. oxalic acid, and, finally, ammonia, until the acid is nearly saturated. The solution is diluted to 250–300 c. c. and a solution of sodium thiosulphate, containing at least 10 parts of the salt to 1 of antimony, is added. On heating, the solution becomes turbid, then a yellow, and, finally, a red precipitate forms; 1–2 c. c. of hydrochloric acid diluted with water is added, and the solution boiled for several minutes. If the boiling is stopped the precipitate deposits and the liquid rapidly clears. A few drops of hydrochloric acid are now added and the liquid again boiled. If the liquid remains clear a little more thiosulphate must be added. If it is milky the metal is com-

pletely precipitated; but if it becomes yellow or red, acid and sometimes thiosulphate, must be added until the turbidity produced on boiling is pure white. The precipitate is filtered, and is of such a character that it can be rapidly washed. Any oxysulphide adhering to the beaker may be redissolved in ammonium sulphhydrate, reprecipitated with hydrochloric acid and added to the rest of the precipitate. The antimony may be estimated as Sb_2S_3 by ignition in a current of dry CO_2 , (it already contains sufficient sulphur) or it may be dissolved in hydrochloric acid and estimated volumetrically.

The filtrate containing the tin is saturated with ammonia while still hot. The precipitate is dissolved in ammonium sulphhydrate, reprecipitated with acetic acid, (hydrochloric acid will not answer) filtered, washed with water containing a little ammonium nitrate, and weighed as stannic oxide. No test analyses given.

Separation of Arsenic Antimony and Tin.—Ad. Carnot, *Comptes Rendus*, 103, 343. The reactions of the alkaline thiosulphates in presence of different acids upon which the author has already founded several separations, may also be used for the separation of arsenic. If thiosulphates are added to a hydrochloric acid solution of arsenious or arsenic acid and the solution boiled, part of the arsenic is precipitated as sulphide and part remains in solution. The same thing happens if the solution is acidified with oxalic acid. The incomplete precipitation is caused by the sulphurous acid produced by the decomposition of the thiosulphate. If sulphurous acid or an alkaline disulphite is first added and then thiosulphate, the arsenic all remains in solution. If sulphurous acid is added to an antimony solution and then thiosulphate, the precipitation of the antimony is somewhat retarded but is still complete. We have thus a means of separating arsenic from antimony.

To a hydrochloric acid solution of antimony and arsenic ammonium oxalate (in absence of tin ammonium tartrate may be used) is added the solution diluted with water, then thiosulphate, in amount proportionate to the antimony present, is

added and finally, a little sulphurous acid or alkaline disulphite, and the solution boiled. As soon as further addition of hydrochloric acid and thiosulphate shows that all the antimony has been precipitated (see preceding article) the solution is filtered and the antimony estimated in the precipitate. The arsenic in the filtrate may be estimated by any of the usual methods.

Antimony and arsenic are often found together in ores, but only occasionally in association with tin. In alloys, arsenic is seldom found, except as an impurity in one of the metals from which the alloy was made, and then only in small quantity. In such cases the antimony is separated by the method above described, leaving arsenic and tin in the filtrate. In this case the filtrate is raised nearly to a boil, a considerable quantity of hydrochloric acid added, and a current of sulphuretted hydrogen passed through it. If the amount of arsenic present is small it will be precipitated in a few minutes and the tin all remain in solution. The solution is kept hot as long as it smells of sulphuretted hydrogen, and then filtered. The sulphide of arsenic is treated with a little hydrochloric acid, to dissolve any trace of tin sulphide, and the filtrate added to the rest of the tin solution. The arsenic in the precipitate and the tin in solution can then be determined in the ordinary way. No test analyses are given.

IRON AND STEEL.

EDITED BY P. W. SHIMER.

Manganese in Steel.—Byron W. Cheever, in a paper read before the Am. Inst. of Min. Eng's (Bethlehem meeting, May, 1886), says of the colorimetric estimation of manganese in steel that, "while it can fairly be ranked with the colorimetric carbon process, and can be used for checking the operations of a steel plant, yet it requires more care to obtain uniform results, and is liable to greater variations from slight causes than the carbon process, and, in my judgment, is not a safe method to employ when exact results are sought.

The following method, which corresponds in many respects with that adopted by others, gives me the most uniform results.

Standard Solution.—Take 1 grm. of steel which contains about one per cent. of manganese (the exact per cent. must have been previously determined); dissolve it in 25 c. c. of nitric acid (1.20 specific gravity), and boil till clear; add 325 c. c. HNO_3 (1.20 specific gravity); cool, and dilute with water so that 1 c. c. will contain 0.01 mgrm. of Mn. After dilution, determine the manganese to see if the solution is correct.

Process.—The amount of steel to be taken will depend upon the percentage of manganese which it contains. I have found that the portion finally taken for oxidation may contain as much as 0.5 of a mgrm. of Mn; therefore, for a steel with 1 per cent. of Mn. take 0.1 grm.; for a steel with 0.5 per cent. of Mn. or less, take 0.2 grm. Dissolve in 15 c. c. HNO_3 (1.20 specific gravity), and boil the solution till clear; cool, and dilute with water to 100 c. c. Take 10 c. c. of this solution in a large test-tube, and add 3 c. c. HNO_3 (1.20 specific gravity); take 10 c. c. of the standard solution in another large test-tube; heat both to boiling; remove from the flame; add to each 0.5 grm. PbO_2 ; bring gradually to a boil, and boil a few seconds; cool till cold; filter through asbestos into

two large carbon-tubes, and dilute the deeper colored solution with water till it corresponds in shade with the lighter.

Precautions.—The amount of manganese in the portion to be oxidized should not exceed 0.5 mgrm.

The solutions must not be too acid, and should have as nearly as possible the same amount of nitric acid. The same amount of peroxide of lead should be added to each, and then raised to a boil, and boiled a few seconds only. If boiled too long some of the permanganic acid will be reduced. I have not found that the mode of heating has any decided effect; but the time of boiling has.

If filtered hot, the color fades more rapidly than when cooled before filtering.

The filtrate must not be diluted too much, since it is difficult to compare pale colors.

The asbestos filters may be used for a number of determinations without change. Before being used, they should be washed with a solution of KMnO_4 , and the latter removed with dilute HNO_3 .

In place of the standard steel solution, I have tried potassium permanganate, and thus far have obtained satisfactory results as to rapidity, but not as to uniform accuracy. I prepare an $\frac{1}{10}$ permanganate solution, and keep it in a dark closet; this solution will hold its strength for a long time. For each day's work, I take 10 c. c. of this $\frac{1}{10}$ solution, and add to it 100 c. c. of water; therefore each c. c. of this second solution contains 0.1 mgrm. of Mn. While the sample under examination is being filtered, I measure into the other carbon-tube 5 c. c. of this standard, add 15 drops of HNO_3 (1.20 specific gravity) and about 10 c. c. of water, and shake. As soon as the filtration is finished, the solutions are compared. The nitric acid must be free from nitrous fumes."

The Estimation of Manganese in Iron and Steel by the Color-Method.—Alfred E. Hunt, (Read before the Am. Inst. of Min. Eng's, at the Bethlehem meeting, May, 1886.) Dissolve 0.1 gm. of the steel in 20 c. c. nitric acid of 1.20 specific gravity in a test-tube, about nine inches long by one inch in

diameter, by the aid of heat, boiling the solution until the carbonaceous matter is entirely in solution and all nitrous fumes are evolved. This usually takes about five minutes at a gentle ebullition. Then add with a platinum spatula about 0.4 gm. of *pure* peroxide of lead to the boiling solution, adding first a small portion of the lead, and as soon as the violent action ceases, an instant later, the rest of the salt, boiling gently but continuously for exactly two and one-half minutes longer, then taking off from the heat and placing the test-tube in a beaker of cold water, out of contact with direct rays of sunlight, and allowing the solution to cool and to settle for about an hour. The clear supernatant solution is then ready to decant off from the lead into the graduating tube and to match by dilution with water with the standard solution containing 0.0001 gm. manganese as permanganate in each c. c. of solution; so that, using one-tenth gm. steel for the analysis, each c. c. of the solution to be determined will represent 0.01 per cent. of manganese when the shades of color match.

The standard solution can be made :

1. From a standard solution of permanganate of potash, or,
2. There can be used for comparison a colored glass rod, of the same bore as the graduated tube, and of a carefully selected shade, which will exactly represent the 0.0001 gm. manganese standard solution in a clear glass tube of exactly the same size as the graduated tube; or,
3. The standard may be prepared by using 0.1 gm. of a standard steel containing a known percentage of manganese, treating it exactly as the unknown sample, and decanting the solution into a similarly graduated tube and diluting with water until the solution has a volume of which the number of c. c. is an equivalent or multiple of the percentage of manganese in the steel—applying the same principle as is used with the standard steels in the Eggertz method for the estimation of carbon.

This method when properly used is at least sufficiently accurate for all practical work, within say .02 per cent. manganese for steels within the range of from 0.15 per cent. to 1.50 per

cent. manganese. It is fully as accurate and can be as safely guarded from error as the Eggertz color-method for the estimation of carbon in steel. The method, however, has many sources of error that must be carefully avoided. Hence, it is the writer's custom, in all important analyses, to make a check analysis by a gravimetric or volumetric method, and also always to make the color-tests in duplicate, in the same way as is pursued when reliance is placed on the color-method for carbon.

The great advantage of the color-method for manganese is that if the result is poor, and any reduction has taken place in the permanganic acid, it can be readily detected by the peculiar duller red color assumed by the solution. Whenever the determination, for any reason, becomes "off color," as the chemists in our laboratory say, we reject the work and start a new analysis. With a little experience in working the manganese color-method solutions that will give erroneous results can be readily detected. This fact, together with the ease with which duplicate results can be obtained, allows the method to be used as an exact one.

The following precautions should be observed:

1. The drillings of steel must have no oil or other extraneous matter with them. Owing to the ease with which permanganate solutions are reduced, it is necessary to have no organic matter present that will not be entirely destroyed by the boiling nitric acid before the addition of the peroxide of lead.

2. The nitric acid must be pure, and especially free from chlorine or nitrous fumes. The acid must be of very nearly 1.20 specific gravity throughout the process, and must not be allowed to become much more concentrated by boiling. To prevent this it is best to cover the mouths of the test-tubes with clean covers of porcelain crucibles during the ebullition. If the acid becomes too concentrated during the boiling, as it is very likely to do if the ebullition becomes very violent and the test-tube be a large one, on addition of the peroxide of lead some of the manganese is transformed into the insoluble binoxide of manganese and is precipitated.

3. The peroxide of lead must be free from color on boiling with the dilute nitric acid, and must be so free from nitrate of lead that it will oxidize all the manganese in the steel to a reasonably permanent permanganic acid. This is a very important point, which, not properly guarded, has occasioned failures and has caused many chemists to condemn the method. In commencing the use of any new lot of peroxide of lead it is a necessary precaution to mix up the salt thoroughly and then to test it by making an analysis with a steel of known composition, comparing it with a standard solution of permanganate of potash, and obtaining a concordant result. The writer has found it necessary to purify his own peroxide of lead and has never yet found any of the best foreign makes called "c. p." to be satisfactory and to give uniformly reliable results. Most of the peroxide of lead sold in the markets is non-homogeneous and contains considerable quantities of nitrate of lead unevenly disseminated in it.

4. The ebullition must not be too violent and must not last over two and one-half minutes. It is necessary to stand by the tubes with watch in hand to take them out when the time is up. Too long boiling invariably gives bad results. The boiling is best done in a water-bath in which chloride of calcium is added to the water to raise its boiling-point.

5. There must not be chlorhydric acid, sulphuretted hydrogen, or other fumes in the air of the room in which the tubes are allowed to stand to cool. It is best not to allow the solution to stand too long, never over two hours before comparison.

6. The writer has no trouble in getting good, reasonably permanent colors, but has never had uniformly satisfactory results by filtering the solution from the peroxide of lead through asbestos, and has consequently preferred to decant off the solution from the lead. When a standard steel is used, having nearly the same percentage of manganese as the sample to be determined, equal amounts of solution, and treatment exactly the same so far as practicable, the error due to the amount of liquid remaining with the lead in the bottom of the tube is comparatively trifling—never over 0.02 per

cent. when the precautions mentioned above are carefully observed.

7. The water used in diluting must be free from organic matter. The ordinary distilled water used in chemical laboratories often contains considerable organic matter, which will rapidly reduce permanganate solutions.

8. The mixing of the color-solutions for comparison can best be done by having the graduated tube provided with a glass stop-cock, or it can be satisfactorily performed by pouring the solution out into a clean beaker and then decanting back into the graduated tube.

Rapid Method for the Determination of Phosphorous.—Mr. F. A. Emmerton, in a paper read before the American Institute of Mining Engineers, describes a rapid and accurate method for the determination of phosphorous. The details of the method, as given by the author, are as follows: “In the case of steel, dissolve 5 gm. in a 6-inch dish, in 75 c. c. HNO_3 , of 1.20 specific gravity. Support a 6-inch watch-glass over the dish, so that the edge of the glass is about $\frac{1}{2}$ inch above the rim of the dish. Boil down rapidly on an iron plate, and heat thirty minutes on the hot plate after the residue looks dry. At the end of this time, the smell of acid should have disappeared. Let the dish cool; add 40 c. c. strong HCl ; put the cover down tight on the dish and heat at a gentle temperature for a few minutes, till the oxide of iron spattered on the cover is softened; then boil down till all but 15 c. c. of the acid is gone. The latter part of the process requires close attention, as it is necessary that at its completion the solution should be very concentrated, and yet that there should be very little chloride dried upon the sides of the dish. Let the dish cool a little; lift up the large watch-glass, and rinse off the lower side of it with 40 c. c. strong HNO_3 , which is allowed to flow into the dish. Then cover the solution with an inverted watch-glass 1 inch smaller in diameter than the dish, so that in the subsequent boiling down of the solution, the liquid condensing on the inner side of the watch-glass will run back to the sides of the dish, instead of to the middle, and

will thus aid in preventing the formation of a crust about the edge of the liquid. Place the dish thus covered on a hot plate, and boil the solution down to about 15 c. c. in bulk. Take the dish from the plate, and move it about so as to moisten with the solution what crust may have formed. In this way, with a little skill, a perfectly clear and highly concentrated solution may be obtained, from which, practically, all the HCl has been expelled.

Dilute this solution, when somewhat cooled, to about 40 c. c. with water, and wash into a 400 c. c. flask, bringing the solution to about 75 c. c. Add strong ammonia, shaking after each addition, to make a thorough mixture of the ammonia with the precipitated ferric hydrate. Continue adding ammonia till the mass sets to a stiff jelly; then add a few c. c. more; shake well; and be satisfied that there is a strong smell of ammonia in excess. Then add strong HNO_3 gradually, shaking well after each addition, until the liquid begins to get thinner. After the precipitate has all dissolved, and the solution shows a very dark color, add a little more HNO_3 , enough to bring the solution to a clear amber color. At this stage the solution will be 150 to 300 c. c., generally about 250 c. c. in bulk. Put a thermometer into the liquid, and observe its temperature; if below 85°C . heat carefully over a lamp-flame till it is raised to this temperature; if above 85°C ., cool to that temperature by immersion of the flask in water. When at 85° , add at once 40 c. c. of molybdate solution.* Close the flask with a rubber stopper; wrap it in a thick cloth, and shake up and down violently for five minutes. At the end of this time the precipitate will be all down.

Collect the precipitate on a filter, using the filter-pump, and wash thoroughly with HNO_3 , diluted with fifty times its bulk of water. No difficulty is experienced in getting practically all of the precipitate from the flask to the filter. If a thin film of the precipitate should adhere to the walls of the flask, it may be removed by a portion of the ammonia used in dissolv-

* The molybdate solution used is made by dissolving 100 gms. molybdic acid in a mixture of 300 c. c. strong ammonia and 100 c. c. water, and pouring this solution into 1250 c. c. HNO_3 , of 1.20 specific gravity.

ing the yellow precipitate previous to the reduction with zinc and sulphuric acid.

Have ready a 500 c. c. flask in which have been put 10 gm. granulated zinc roughly weighed out. Put the moist filter with precipitate on a funnel in the neck of this flask; punch a hole in the point of the filter, and wash the precipitate into the flask with ammonia, 1 in 4. This can be done thoroughly without using more than 30 c. c. ammonia. Then pour into the flask 80 c. c. hot dilute sulphuric acid, 1 in 4, and cover the neck with a small funnel. Heat quickly on an iron plate till rapid solution of the zinc begins, and then heat gently for ten minutes. At the end of this time, the reduction is complete. To separate the liquid from the undissolved zinc, pour it through a large folded filter; rinse the flask with cold water, and, after these washings have run through, fill up the filter once with cold water. The filtration on a large folded filter exposes the liquid but a very short time to the air. The zinc is decanted into the filter with the liquid, on which it continues to act till the latter has drained through.

The filtrate, amounting to 400–500 c. c., is then ready for titration with permanganate, which is run in till the liquid is colorless. During the reduction of the MoO_3 the liquid takes on successively the colors, pink, plum, pale olive-green, and dark olive-green, the darkness of the final color depending on the amount of MoO_3 reduced. The moment the reduced liquid is exposed to the air on the filter, it loses its green, and takes on a port-wine color, but this change does not seem to be due to an appreciable amount of oxidation, the oxidation of the reduced liquid taking place slowly, as was shown by Werncke.

In titrating the wine-color becomes fainter, and finally disappears, leaving a perfectly clear liquid, in which one drop of permanganate produces a plain pink color.

I use a permanganate solution of which 1 c. c. = .006141 iron; .9076 times this value gives its strength in terms of molybdic acid = .005574; and 1.794 per cent. of this is its value in phosphorus = .0001."

The author made careful experiments on the accuracy of

the method, with respect to the completeness of the precipitation of the phosphorous; the relative proportion of phosphorous and molybdic acid in the precipitate obtained in this way; the limits of temperature between which a uniform precipitate may be obtained; the time required for the complete reduction of the MoO_3 by zinc; and the comparative results obtained by this and the magnesia method; the results of which experiments are embodied in the method as described.

The following are some comparative results on ores:

No. of experiment.	Phosphorous by magnesia.	Phosphorous by titration.
1	.197	.198
2	.067	.065
3	.188	.187
4	.096	.098
5	.061	.061
6	.103	.101
7	.029	.030
8	.032	.033
9	.132	.135
10	.026	.025
11	.057	.057
12	.026	.025
13	.077	.081
14	.047	.046

Mr. H. B. Nye, chemist to the North Chicago Rolling Mill Company, also gives the results of confirmatory experiments on this method. He says, further: "In the case of irons I dissolve 5 gm. and get the HNO_3 solution as described above. I wash this into a graduated 100 c. c. flask, dilute to the mark, mix, pour through a dry filter into a dry bottle, using the filter-pump. From the filtrate I draw off 80 c. c. with a pipette, and in this amount, holding 4 gm. of the iron taken for analysis, I finish the determination. In this way, what may be a tedious filtration and washing is avoided, and the bulk of the solution is kept constant.

In the case of ores, I dissolve 10 gm. in HCl , evaporate to dryness, take up with HCl , evaporate to small bulk, and ex-

pel the HCl by boiling down with 40 c. c. strong HNO₃. With this method I never take more than three hours for a determination in iron or steel; do not need more than two hours, and, with close attention, have made accurate determinations in one hour and fifty minutes.

I have used a mechanical device for shaking the flasks during the precipitation, which is very convenient, especially when a great many determinations have to be made. It consists of a box, the inside of which is about $\frac{3}{4}$ inch higher and $\frac{1}{2}$ inch wider than the stoppered flask. It has a door in front, which closes tight; a leather strap having a loop in the middle just large enough for the neck of the flask to pass through, is placed in the box, so that one end is fastened permanently to the box on one side, and the other passes out on the other side and is fastened on the outside of the box by a screw clamp. In putting the flask into the box, the neck is passed up through the strap, and the free end of the strap on the outside is pulled down tight, till the flask is pressed firmly on the bottom of the box. The strap is then held securely in place by the compression of the screw clamp.

The box, which may have two or more such compartments in it, is mounted on an upright, which slides between guides, and is given an up-and-down stroke of about 6 inches, by a simple arrangement of pulleys and a crank. When run at about 100 strokes per minute, it gives a very satisfactory shaking. It takes only a few seconds to fasten a flask into the box, and as many more to take it out. This appliance thus saves considerable time and exertion.

The box prevents any considerable loss of heat during the shaking, so that the liquid is kept, during the precipitation, between the limits of temperature which insures a precipitate of correct composition."

Influence of Copper on the Estimation of Sulphur.—Wm. F. Brugman, Chemist, Scranton Steel Co., gives in the October, 1886, number of the School of Mines Quarterly, the results of some experiments in the determination of sulphur in iron and steel containing copper. He sought to deter-

mine whether or not the presence of copper in the solution in which H_2S is being evolved, causes the precipitation of any sulphide of copper. The following results lead him to conclude that copper exercises no deleterious influence, and may safely be disregarded when present to the amount of 1 per cent.

A sample of pig iron containing .835 per cent. Cu., gave by the "Aqua Regia Method," .228 per cent. S.

Fused with Na_2CO_3 and reprecipitated, .226 per cent. S.

Sulphur in same iron by " H_2S Method," .228 per cent. S.

A pig iron free from Cu., gave, " H_2S Method," .025 per cent. S.

Determination repeated, after adding .035 Cu. in the form of chloride, .023 per cent. S.

Sample of steel containing .70 per cent. Cu. gave (H_2S Method), .086 per cent. S.

Repeated, adding to drillings .054 CuO, gave .087 per cent. S.

Sample of steel, free from Cu., gave, same method, .046 per cent. S.

Same, after adding .054 Cu., .048 per cent. S.

Sulphur in Iron.—Mr. T. Wiborgh, Chem. News, 54, 158, translated from Jern Kontoret's Annaler, 1886, p. 105, by J. Crom, gives the details of a carefully worked-out method for the colorimetric estimation of sulphur in iron. The basis of the method is that the gases evolved by the solution of iron in diluted sulphuric or hydrochloric acid pass through a cloth impregnated with a metallic salt, and through the action of the sulphuretted hydrogen, a metallic sulphide is formed which colors the cloth more or less intensely according to the amount of sulphur in the iron. The author found a solution of cadmium nitrate or acetate to give the best results. The method is described in minute detail, and is no doubt a most useful one in cases where all the sulphur is evolved as H_2S when dissolved in dilute HCl or H_2SO_4 .

As is well known, many American pig irons contain a very

notable proportion of the total sulphur in the residue insoluble, in dilute HCl, which, not being evolved as H_2S , does not contribute to the color of the cloth.

Determination of Aluminium in Presence of Large Proportions of Iron.—Robert T. Thomson, Chem. News, 54, 252. In testing for minute proportions of aluminium in presence of a large proportion of iron, was led to try the best-known methods, namely, by boiling with a large excess of caustic soda or potash and subsequent precipitation in the filtrate from the peroxide of iron ; and by direct precipitation with thiosulphate of sodium. In the latter case, only about 90 per cent. of the total aluminium present was obtained when working on a solution containing 100 parts of iron to 1 part of aluminium. But the failure of the caustic alkali method was more striking, as not a trace of alumina could be detected in the soda filtrate.

Since both of these methods had to be rejected, he devised the following method, which gave satisfactory results :

The iron, if in the ferric state, is first reduced to the ferrous conditions by passing a current of sulphurous acid through the solution. The excess of acid is boiled off, the mixture cooled, and at least as much phosphoric acid, or phosphate of ammonium or sodium, added as will be equivalent to the alumina present. It is desirable to add a large excess of phosphoric acid, as the alumina may not be completely precipitated if it has not at least its own equivalent of the former. One drawback to the unlimited use of phosphoric acid is that if manganese is present it will be thrown down, but if the quantity of the former is limited the latter will remain in solution.

When manganese is present in quantity it is advisable to employ the alternative method of precipitation to be described further on. Ammonia is now added until a faint permanent cloudiness is formed ; then excess of ammonium acetate, which throws down the alumina as phosphate. The precipitate always contains some ferric phosphate, which forms from any traces of ferric salt which may have escaped reduction, and

11111111

from the oxidizing action of the air during filtration. The great bulk of the iron, however, remains in solution in the ferrous condition. The precipitate is now collected on a filter, washed two or three times with water, and dissolved by passing dilute warm hydrochloric acid through the filter. If it does not seem sufficiently free from iron, the solution thus obtained should be put through the same process as has just been described, beginning at reduction with sulphurous acid. When filtered rapidly I have had as little as 0.1 grm. of peroxide of iron in the aluminium phosphate, and in no case have I required a reprecipitation. It is well to reduce the iron as much as possible.

An alternative method of getting rid of the great proportion of iron, is to add ammonia to the reduced solution till a slight cloudiness is formed, then excess of ammonium acetate, and boil for a few seconds. The whole of the alumina and a portion of the iron is precipitated, and are collected in a filter. No phosphoric acid is added in this case, and manganese remains in solution. More iron is brought down than in the first described cold method, and, when only minute quantities of alumina are expected, a second reduction and precipitation will most likely be necessary.

After obtaining a satisfactory precipitate (whichever method has been adopted), it is dissolved in hydrochloric acid, boiled with a little nitric acid to oxidise any proto-salt of iron, nearly neutralized with pure caustic soda, and added to a considerable excess of the latter in a nickel basin. The mixture is boiled for a short time, filtered, the filtrate acidified with hydrochloric acid, and a large excess of phosphoric acid or phosphate of ammonia or soda added. I have found that the presence of at least two equivalents of P_2O_5 to one of Al_2O_3 are necessary to give rise to the normal phosphate of aluminium ($Al_2P_2O_7$). The latter is now precipitated by adding ammonia till a slight cloudiness is produced, and then excess of acetate of ammonium. Or, the precipitation may be effected by a simple neutralization with dilute ammonia till a red reaction ceases to be obtained with lakmoid paper. The aluminium phosphate is now collected in a filter, washed thoroughly with

a hot 1 per cent. solution of ammonium nitrate, containing about 0.1 grm. of the di-acid ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) per liter, dried, ignited and weighed. If the aluminium phosphate is washed with water it partially loses its gelatinous form, and becomes tedious to filter. But besides this the precipitate is decomposed to a considerable extent, and a portion of the phosphoric acid passes into solution. For these reasons the precipitate must be washed in the manner described, when pure $\text{Al}_2\text{P}_2\text{O}_8$ is weighed, and may be calculated to alumina or aluminium as required.

The following are results obtained by the above process in solutions containing 3 gms. of metallic iron. To the iron solution a weighed quantity of pure ammonia alum was added:

Grm. of Al_2O_3 added.	Grm. of $\text{Al}_2\text{P}_2\text{O}_8$ obtained= $\text{Grm. of Al}_2\text{O}_3$ obtained.	
0.0340	0.0800	0.0336
0.1135	0.2695	0.1132
0.1135	0.2703	0.1136

The presence of titanium is not injurious in the above process, as only slight traces of titanous acid are dissolved by strong caustic soda.

Phosphorous in Steel.—N. Huss, Zeit. anal. Chemie. 25, 319, describes a modification of the Sonnenschein method for the determination of phosphorous. The experiments detailed were made upon Thomas steel practically free from silicon.

The author found that the presence of any undestroyed carbonaceous matter in the solution to be precipitated by ammonium molybdate causes the reduction and precipitation of part of the molybdic acid as a lower oxide. This lower oxide is subsequently dissolved in ammonia along with the phosphomolybdate of ammonium, coloring the solution more or less yellow. On adding magnesia solution, the lower oxide is carried down with the phosphate of magnesia and ammonia, and the pyrophosphate obtained on ignition is more or less colored.

The contamination by molybdenum may be avoided by adding a few drops of bromine to the slightly ammoniacal solution of the yellow precipitate, letting it stand a few minutes,

and then adding ammonia to alkaline reaction. The lower oxide is converted into molybdic acid which is not carried down with the precipitate by magnesia, and the latter is obtained perfectly white on ignition.

The method used by the author is the following: 10 gms. steel are dissolved in 200 c. c. HNO_3 , 1.20 sp. gr., and the solution is boiled 15 minutes. When cold, 100 c. c. of 28.65 per cent. solution of NH_4Cl is added. This is the amount calculated to convert the solution into one of ferric chloride and ammonium nitrate. 50 c. c. of a water solution of ammonium molybdate containing 20 per cent. of the crystallized salt is run into the solution from a burette. The solution is kept at the temperature of 50° for 15 minutes, when the precipitation is said to be complete. The yellow precipitate is washed first with a dilute nitric acid solution of ammonium molybdate, and finally 4 or 5 times with warm water containing one per cent. of HNO_3 . The filter is spread out in a watch-glass and dried at 80° . The yellow powder is brushed into a weighed porcelain crucible in which the paper has previously been incinerated at as low a temperature as possible. The precipitate is again heated to 80° for a few minutes, allowed to cool and weighed. 1.63 per cent. of its weight is phosphorous.

MINERAL ANALYSIS.

EDITED BY JOHN EYERMAN.

Nephrite from Asia.—A. B. Meyer, (Zeit. Kryst. Min. 10, 612) has analyzed Nephrite from Yunnan, Asia (a new locality). Analysis gave

SiO_2 .	Al_2O_3 .	FeO .	CaO .	MgO .	H_2O .	Total.
56.58	0.92	4.12	12.92	21.65	3.25	99.44

Altered Cordierite.—E. Scacchi, (Atti. Acad. Lincei, II, pp. 183) describes altered cordierite, occurring in liparite, from Rocca Tederighi, Tuscany. The mineral is found in green prisms. An analysis gave

SiO_2 .	49.65	CaO .	3.95
Al_2O_3 .	27.41	MgO .	1.23
Fe_2O_3 .	8.89	H_2O .	8.38
			<hr/> 99.51

NOU

Pectolite from Alaska.—H. Fischer (Zeit. Kryst. Min. 10, 614) has analyzed apple-green pectolite from Port Barrow.

SiO ₂ .	CaO.	MgO.	Na ₂ O.	Al ₂ O ₃ .	H ₂ O.	Total.
53.94	32.21	1.43	8.57	0.58	4.09	100.82
Sp. Gr. 2.873.						

Meteorite Iron from South Carolina.—Mr. W. E. Hidden describes (Sch. Mines. Quart. 8, 1) a meteorite (cuboidal) found in Laurens Co. S. C., in 1857, an analysis of which by J. B. Mackintosh, shows high percentages of Nickel and Cobalt.

Iron	85.33
Nickel	13.34
Cobalt	0.87
Phosphorous	0.16
Carbon	traces
Sulphur	traces
	<hr/>
	99.70

By etching with nitric acid, the Widmannstätten figures were brought out. The writer then describes a broad double line running over the entire exterior of the mass. From this line, branch smaller lines, pointing upwards at an angle of 70°, diverging, right and left at the same inclination, showing that twinning has occurred parallel to an octahedral face.

Composition of the Mineral Bruiachite from Loch Bruichlish.—W. J. Macadam describes (Min. Mag. VII, 32, 30.) Bruiachite found by Mr. Th. D. Wallace, as a clear and beautifully crystalline mineral and very friable. An analysis, average of six tests, gave

Calcic oxide	87.045
Sodic oxide	1.697
Ferric oxide	0.595
Fluorine	10.006
Silica	0.542
	<hr/>
	99.885

Mimetesite from Puy de Dome.—A. Domour (Zeit. Kryst. Min. 10, 627) analyzed botryoidal mimetesite of a grayish color from Pontgibaut, with the following results :

As ₂ O ₅ .	P ₂ O ₅ .	PbO.	CaO.	Cl.	Pb.	Total.
19.65	3.44	63.25	3.46	2.57	7.49	99.86
Sp. gr. = 6.65						

Arsenolamprite.—C. Hintze (Bonn) describes (Zeit. Kryst. Min. 11, 638) a mineral indetical with the so-called arsen-glany of Briethaupt, Sp. gr. 5.30, by pycnometer 5.54. This latter corresponds to that by Breithaupt to the Saxon mineral, which contained bismuth. Hardness between 2 and 3. Well defined cleavage, color gray to bluish ; streak black. Analysis of two specimens by Dr. Klinger gave

Arsenic	98.14	98.43
Iron	1.92	1.00
Silica	0.55	0.05
	<hr/>	<hr/>
	99.61	99.48

Agalmatolite from near Loch Maree, Ross-Shire, Scotland.—W. Ivison Macadam describes (Min. Mag., VII, 32, 29.) Agalmatolite from Creag Mhòr Thollie, Loch Maree. The mineral according to Macadam has no very definite composition, but can be produced in the presence of an excess of silica. He further thinks that this mineral would fall under the title of "Siliceous Agalmatolite." An analysis gave

Silica	63.256	Calcic Oxide	0.213
Alumina	26.414	Potassic Oxide	6.413
Ferric Oxide	1.832	Sodic Oxide	0.157
Magnesian Oxide	1.105	Water	0.508
			<hr/>
			99.898

Bismuth from Sweden.—L. J. Igelström, (Jahrb. f. Min., 1886, Ref. 398–399) has observed native bismuth and bismuth-glance associated with chalcopyrite in Säjnsnäs, Dalecarlia.

Analcite from Blagodat.—P. Nikolaieff has analyzed (Zeit. Kryst, Min., II, 392) analcite from Blagodat; I, crystalline; II, compact:

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	H ₂ O	Total
I.	54.42	22.89	0.40	0.87	tr.	13.00	—	8.13	99.71
II.	55.28	21.21	0.93	3.70	0.39	8.93	2.73	5.01	98.18

Sp. gr. I.—2.277. II.—2.481.

Turkestand Apatite.—P. V. Jeremieff and P. D. Nikolaieff (Zeit. Kryst, Min., II, 389) have analyzed apatite from the banks of the Maiden-tal river.

Insoluble

residue.	F	Cl	P ₂ O ₅	CaO	MnO	Fe	Total
0.12	3.64	tr.	41.93	55.29	0.18	tr.	101.16

Sp. gr.=3.199.

Rinkite and Polylithionite from Greenland.—J. Lorengen (Jahrb. f. Min. 1886, i, Ref., 404) describes Rinkite and Polylithionite from Kangerdluarsuk, Greenland.

Rinkite is Monoclinic; axes— $a:b:c=1.56878:1:0.292199$
: $\beta=88^{\circ} 47'$.

F	SiO ₂	TiO ₂	<u>CeO, LaO, DiO</u>	YO	FeO	CaO	Na ₂ O	Total
5.82	29.08	13.36	21.25	0.92	0.44	23.26	8.98	103.11

$2R^{II}R^{IV}O_8 + NaF$.— R^{II} is Ce, La, Di, Y, Fe, Ca, Na₂, and R^{IV} is Si and Ti

Polyolithionite—Analysis resulted,

F	SiO ₂	Al ₂ O ₃	FeO	K ₂ O	Na ₂ O	Li ₂ O	Total
7.32	59.25	12.07	0.93	5.37	7.63	9.04	101.11*

Idocrase from Almerge and Condove.—A. Cossa, (Zeit. Kryst. Min. II, 408) describes vesuvianite associated with bornite, occurring in the mountains above Almerge and Condove. Analysis resulted

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	H ₂ O	Total
37.46	15.51	5.39	35.98	1.97	3.40	99.71

Sp. gr.=3.39.

*101.11 in original article, result should be 101.61.

Argyrodite and Arminite (New Minerals.)—A. Weisbach (Jahrb. Berg-Hüttenwesen, '86) describes and names two new minerals, as above.

Argyrodite, in which the new element Germanium occurs, crystallizes in the monoclinic system, the crystals are generally small; axial relation is $a : b : c$ (vert.) = $1 : 1.67 : 0.92$. twins are common; specific gravity 6.093—6.111; hardness, 2.5; streak grayish black, shining; luster, metallic, cold steel gray, with tinge of red on the fresh surface; no cleavage and rather brittle. Argyrodite occurs as a crust upon marcasite, siderite and argentite, and associated with other silver minerals at the Himmelfürst mine, Freiberg. Analysis by Winkler gave

S	Ge	Ag	Fe	Zn	Total
17.13	6.93	74.72	0.66	0.22	99.66

Arminite is a hydrous copper sulphate incrusting porcelain-jasper from Planitz, near Zwickau.

The material analyzed was small and somewhat impure. Analysis also by Winkler:

SO ₃	CuO	<u>Fe₂O₃, Al₂O₃</u>	CaO	Total
24.43	56.81	0.35	0.56	= 82.15

Assuming the loss to be water, the formula is $\text{Cu}_5\text{S}_2\text{O}_{11} + 6 \text{H}_2\text{O}$.

Crocidolite from Orange River, Africa.—A. Renard and C. Klement (Zeit. Kryst. Min. II, 442) give analyses of crocidolite and fibrous quartz from South Africa. An analysis of crocidolite afforded

SiO ₂	Fe ₂ O ₃	FeO	CaO	MgO	Na ₂ O	K ₂ O	H ₂ O	Total
51.89	19.22	17.53	0.40	2.43	7.71	0.15	2.36	101.69

Xenotime from Minas Geraes, Brazil.—H. Gorceix (Compt. Rend., 102, 1024) gives an analysis of xenotime from Dattas, south of Diamantina.

P ₂ O ₅	<u>Y₂O₃, Er₂O₃</u>	Insoluble	Total
35.71	63.48	0.62	99.81

Topaz from Tasmania.—A. V. Groddeck (Zeit. Kryst. Min. II, 440) gives an analysis of compact topaz from Mt. Bischoff, Tasmania.

SiO ₂	Al ₂ O ₃	CaO	F	Total	Sp. gr.
33.24	57.02	0.83	17.64	108.73	3.456

Haemafibrite and Haematolite.—E. Bertrand (Jahrb. f. Min., 1886, 1, 12–13) has analyzed Haemafibrite and Haematolite, from the Nordmack mine, Wermland, Sweden.

Haemafibrite is rhombic. An analysis resulted :

As ₂ O ₅	MnO	FeO	MgO	CaO	H ₂ O	Total
29.94	46.98	4.65	2.00	1.50	14.93	100.00

2 (3 MnO, As₂O₅), 7 (MnO, H₂O) 6 H₂O.

Analysis of Haematolite gave :

As ₂ O ₅	MnO	FeO	MgO	CaO	H ₂ O	Total
25.70	34.55	13.95	8.10	2.52	16.08	100.90

2 (3 MnO, As₂O₅), 8 (MnO, H₂O) + 6H₂O.

Haematolite crystallized in the monoclinic system.

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Germanium.—Winkler (Journ. prakt. Chem. N. F. 34, 177) has determined the atomic weight of Germanium by titrating the chlorine in the tetrachloride, GeCl₄, according to Volhard's method. His figures are as follows :

0.1067	0.076112	0.076112	0.076112	0.076112	0.076112	Ge=72.31
.1258	"	"	"	.083212	"	72.41
.2223	"	"	"	.047136	"	72.27
.2904	"	"	"	.192190	"	72.29
Mean,						72.32

Unfortunately, Winkler does not state what values he assigned to the atomic weights for silver and chlorine in making his computations.

In the same paper Winkler cites some specific heat determinations made by Wilson and Petterson. For metallic Germanium we have—

Sp. Heat.	0.0737[0°-100°]	.0772[0°-211°]	.0768[0°-301.5°]	.0757[0°-440°]
Atomic Heat.	5.33.	5.58.	5.55.	5.47.

The specific heat of GeO_2 , between 0° and 100°, is 0.1293.

The vapor density of the chloride was from 7.43 to 7.46, while the theoretical value is 7.40. The identity of Germanium with Mendelejeff's ekasilicium is demonstrated.

Tungsten.—The atomic weight of tungsten has been redetermined by Waddell (Am. Chem. Journ. 8, 280), who took elaborate precautions to free his material from silica and molybdenum. Tungstic oxide, purified by a series of fractional precipitations, was reduced in hydrogen, with results as follows. $\text{O}=16$.

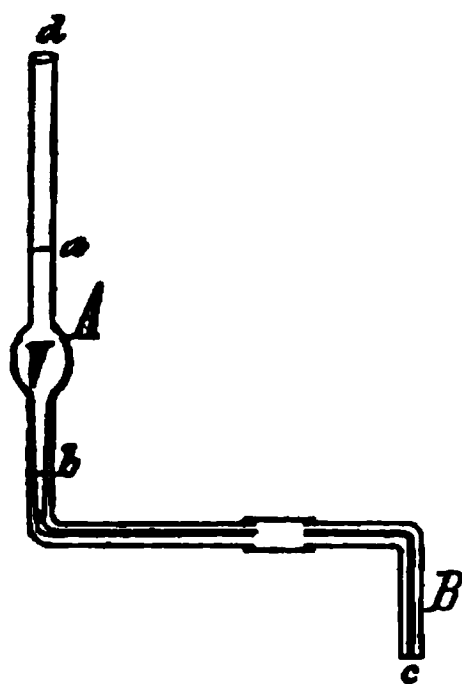
1.4006	gram.	WO_3	gave	1.1115,	W	W=184.55
.9900	"	"	"	.7855,	"	184.37
1.1479	"	"	"	.9110,	"	184.59
.9894	"	"	"	.7847,	"	184.00
4.5639	"	"	"	3.6201,	"	183.67

Two specific gravity determinations for metallic tungsten, one of metal not specially freed from molybdenum, and one which was considered pure, gave 18.25 and 18.77 respectively.

ORGANIC ANALYSIS.

A Method for Distinguishing between Albuminoids, Gelatine and Peptones, has been found by G. Bödlander and J. Traube (Ber. d. deut. chem. Ges., 19, 1871) Musculus first observed that many bodies dissolved in water have a great influence upon its rise in capillary tubes, while others have very little effect. He divided substances according to their behavior in this way into the "capillary active" and "capillary inactive." Traube has however shown (J. pr. Chem. N. F., 31, 177) that no such sharp line can be drawn, as the two classes pass imperceptibly into each other.

Traube has shown (Jour. f. prak. Chem., N. F., 34, 292) that the volume of the drops which form upon the circular horizontal end of a capillary tube are not exactly proportional to the height to which the liquid rises in a capillary.



The determination is made as follows: The apparatus consists of the tube *A*, with two marks *a* and *b*, connected by a rubber tube with the capillary tube *B*. The end of *B* at *c*, has a radius of 3 mm. and is greased on the sides, near the end surface. The tube *A* is now filled to *a*, either by suction or at *d*, and the number of drops made by volume *V* (from *a* to *b*) is counted. To show the uniform results obtained by this method, the number of drops in volume *V* water at 17° was determined as follows:

	I	II	III	IV	V
Z (=number of drops)=	$47\frac{3}{4}$	$47\frac{1}{2}$	$47\frac{1}{2}$	$47\frac{3}{4}$	$47\frac{1}{2}$

The maximum error is therefore scarcely $\frac{1}{4}$ drop in 50. With an albumin solution scarcely any effect is produced and the same may be said of gelatine, while peptones have a very decided effect. 2 per cent. of albumin peptone has a greater effect in increasing the number of drops than 2 per cent. of albumin. It will therefore be easy to estimate the amount of peptones in wine even in presence of albumin since normal wine has nearly the same capillarity constant as water.

It would probably be easy to extend this principle to other determinations.

Opium Analysis.—C. M. Stilwell, Amer. Chem. Jour. 8, 295. The method which Stilwell proposes is a modification of Dr. Squibbs' process.

Sampling.—In sampling such a complex substance as opium great care must necessarily be taken, as the percentage of morphia varies perceptibly in different lumps. The author proposes to cut a small piece from the middle of every tenth lump in a case; care must then be taken that these pieces do not lose moisture by exposure. In preparing these pieces for analysis, they are worked with the hands until a section cut anywhere from the piece shows a perfectly homogeneous surface, care being taken that no loss of moisture takes place.

It is then put in a suitable box or bottle to be kept for analysis.

If the sample be hard and dry and cannot be mixed by the above method it is broken up coarsely, an average portion taken for moisture, and an average of the remainder dried in the water bath until it is possible to grind it in a mortar to a sufficiently fine powder. The moisture and the morphia are determined in the prepared sample. Then by calculation the result is reduced, first, to the amount present on a dry basis, and then to that present in the original sample.

Moisture.—Two separate portions of the average sample, from 6 to 8 grams each, are weighed and dried at 100°C. From samples prepared as above described duplicates for moisture will agree very closely. For example:

1	24.70	23.13	22.90	20.30	17.90	20.60
2	24.70	23.40	22.70	20.60	17.50	20.70
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Average	24.70	23.26	22.80	20.45	17.70	20.65

Determination of the Morphia.—Weigh off a portion of the average sample, using about 10 grams, noting the exact weight of the portion taken. Place the weighed portion in a strong beaker; add 100 c. c. water, and then, with a glass rod fitted at the end with a piece of thick rubber tubing, rub and break the lump of opium until it is thoroughly disintegrated; satisfactory results are only obtained by letting the opium stand some hours, best over night, in order that the morphia may be thoroughly extracted. After the morphia has all been extracted, filter off the solution into a graduated cylinder, and wash the filter and residue with pure water until the filtrate measures about 120 c. c.; set this solution aside and return the residue to the beaker by means of a small spatula; add 30 c. c. of water, and shake well; filter this solution through the same filter. Again return the residue and treat with 20 c. c. of water and filter, and, finally, repeat the treatment with 20 c. c. more. It is best to let the water stand on the residue ten minutes or so before filtering, and press out the insoluble

residue each time it is filtered. In this way the above treatment will exhaust 10 grams of any opium.

Evaporation of the Aqueous Solution of Morphia.—The washings measuring about 70 c. c. are placed in a porcelain capsule of 6 to 8 inches in diameter, evaporated over a water-bath at a heat below boiling; in this way the danger of injury by heat to the alkaloid is reduced to a minimum. Evaporate to about 25 c. c. and then add the first portion of the solution, washing out the cylinder with a little water and evaporate the whole to about 25 c. c. Cool the capsule and contents and add 5 c. c. of alcohol (sp. gr. 0.82) and stir until a uniform solution is obtained. If a precipitate forms as sometimes happens, it is not necessary to filter, as it is removed in a subsequent treatment, and is not reckoned as morphia. Pour the solution into an Erlenmeyer flask fitted with a good velvet cork, using a flask of about 2 inches diameter at the bottom and 5 inches high, and wash the capsule with about 5 to 10 c. c. of water. Add 5 c. c. more of alcohol, and mix the liquids thoroughly by rotating the flask, and not by an up and down movement. Then add 30 c. c. ether and again mix well by rotating.

Precipitation of the Morphia.—Add 4 c. c. of ammonia solution of 10 per cent. (sp. gr. 0.960), wet the cork with ether, and insert at once into the flask. Shake the flask strongly with an up and down motion until the crystals begin to separate. This will occur in a moment or two if everything has been properly carried out. Then set the flask aside for twelve hours, to complete the crystallization. By vigorous shaking the crystals are obtained in a fine granular condition, easily washed and separated from the flask.

Filtering off the Morphia.—Filter off the ether as closely as possible into a tared filter of about 4 inches in diameter, well wetted with ether. Wash several times with 10 c. c. of ether. If some of the aqueous solution pass into the filter with the ether it is of no importance. The washing with ether is followed, first, by a thorough washing with a solution of "Morphiated Spirit" (made by mixing one part of Ammonium Hydroxide, sp. gr. 0.880 with twenty parts of

alcohol and saturating with morphia, the solution contains 0.33 per cent. of morphia), thus removing all the coloring matter and soluble resin. This is followed by a thorough washing with "Morphiated Water" (made by saturating water with morphia; this solution contains 0.04 per cent. of morphia) until all extractive matter is removed; now let the filter drain for a few minutes and wash twice with 10 c. c. "Morphiated Spirit." Let drain for a few minutes, keeping the funnel covered, then wash twice with 10 c. c. of ether, to remove the last trace of Narcotine. Dry at 100° C. and weigh.

The chief impurity contained in the crystals of morphia thus obtained is meconate of lime, together with some organic matters insoluble in water and alcohol.

In order to get rid of these, the crystals are carefully brushed from the filter, treated in a small beaker with hot alcohol of 95 per cent. This dissolves all the morphia; leaving the insoluble organic matter and meconate of lime. The hot alcoholic solution is run through the filter which contained the morphia, the small portion of the crystals remaining on the paper being thus drenched with hot alcohol and the morphia dissolved. The filter is then dried with its balanced paper and the amount of residue obtained. This is subtracted from the original weight of the precipitate, and the remainder calculated into the per cent. of morphia. The composition of the morphia crystals on which the calculation for the per cent. is based is $C_{24}H_{19}NO_6 + 2 \text{ aq}$, containing 5.94 per cent. of water of crystallization. At 120° C. the water is expelled, and at a higher temperature the crystals become carbonized.

In regard to the accuracy of the process thus modified, he gives the following results: "A lot of opium very uneven in quality was sampled by one of our men and I made the analysis, obtaining, water 24.30; morphia 11.75 per cent. Three months afterwards the same lot was re-sampled by myself and one of our men, and the resulting sample analyzed by me, in duplicate, using different weights of opium for each analysis. The results obtained were, water 24.70; morphia 11.70 and 11.82; average 11.76 per cent.

WATER, AIR AND FOOD.

The Estimation of Free Oxygen in Water.—Katherine J. Williams and W. Ramsey, Jour. Chem. Soc. **49**, 751. An examination of Schützenberger's method for determining free oxygen by sodium hyposulphite and indigo. The apparatus used consisted of a wide mouthed bottle closed with a cork in which five holes had been bored. Through two of these passed the exit-tubes of burettes containing, respectively, indigo solution and hyposulphite, by means of the usual arrangements. These burettes could be filled from the stock bottles by means of T tubes from below. The third hole served to introduce hydrogen from a continuous supply apparatus. Through the fourth hole a doubly-bent tube was inserted, serving, when drawn up above the level of the liquid in the bottle, as an exit-tube for the hydrogen, and when pushed down as a means of emptying the bottle. A tube, provided with a stop-cock and connected with a reservoir, passed through the fifth hole, and was used in introducing the water to be tested.

The hyposulphite solution was made by saturating a strong solution of 100 gms. sodium sulphite with sulphur dioxide, adding 20 gms. zinc-dust, and cooling. Milk of lime prepared from about 20 gms. quicklime was added, and the resulting solution was then transferred to the stock bottle which was fitted up like a wash bottle, the liquid being covered with a layer of benzine. This solution can be kept for at least two months. For use this solution is diluted so that 7 to 9 c. c. is equivalent to 10 c. c. copper solution. The copper solution was made by dissolving $4.63 \text{ CuSO}_4 + 5\text{H}_2\text{O}$ in water, adding ammonia until redissolved and diluting to a liter. The hyposulphite is added until the copper solution becomes yellow: 10 c. c. copper solution = 1 c. c. oxygen gas at normal pressure and temperature.

The indigo solution recommended by Schützenberger was found to be too strong, and the best results were obtained by a solution of such strength that 20 c. c. were decolorized by 10 c. c. hyposulphite. The determinations were made at the

ordinary temperature since it was found that the only difference was in the slightly longer time required.

"The experiments were conducted as follows: Having expelled all air from the bottle by a current of hydrogen, the water to be tested was admitted through the bulb-tube; a few c. c. of indigo was added to tinge the water, and the hyposulphite was added from the burette until the blue color changed to yellow. On standing for some minutes, it again changed to blue. More hyposulphite was added from time to time until the solution remained permanently yellow. The indigo having been previously compared with hyposulphite, the amount of the latter equivalent to the small quantity of indigo added was deducted from the total amount used; and the remainder was assumed to have reacted with the free oxygen in the water. This is the first method given by Schützenberger."

The other method employed was to add a considerable amount of indigo to about 100 c. c. of water in the bottle, and to destroy its color with hyposulphite. The water to be tested was then added and the resulting blue color again destroyed. In this case the amount of oxygen is calculable directly from the amount of hyposulphite taken.

The results given by method 2, which the authors prefer, because it requires less time than the first, are as follows: Bristol tap water shaken with air being used.

By Gas Analysis.	With Hyposulphite.
5.63 c. c. per liter.	Series 1, mean of 4, 5.564 c. c.
5.26 " "	Series 2, " 6, 5.229 "
5.454 " "	Mean of both 5.402 "
5.263 " "	
mean 5.402 " "	

Absorption Tubes for the Estimation of Carbonic Acid in Atmospheric or Ground Air.—Thos. C. Van Nüys, Amer. Chem. Jour. 8, 315. The author having found that the Pettenkofer tubes yielded too high results, concludes that the excess was caused by the solution coming in contact with air while being titrated. For a description of the apparatus he

employed to obviate this difficulty I must refer the reader to the original paper.

Determination of Organic Carbon in Water.—A. Herzfeld, Ber. d. deut. chem. Ges., 19, 2618. Degener and Maercker have estimated the organic carbon contained in water by oxidizing with chromic and sulphuric acids and collecting the carbon dioxide. The author finds that with waters containing chlorides this leads to erroneous results, as chlorine is formed and passes over with the carbon dioxide. To remedy this source of error a tube containing metallic antimony is inserted between the evolution flask and the potash bulb. This absorbs the chlorine. Further he finds the method gives from .2 gm. sodium acetate, working rapidly 0.0840 CO₂, working slowly .1130 CO₂; calculated 0.1294 CO₂.

.1 gm. stearic acid gives (two hours) 0.2628 CO₂; calculated 0.2789 CO₂.

3 gm. phthalic acid (1½ hours) 0.644 CO₂; calculated .704 CO₂.

AGRICULTURAL CHEMISTRY.

EDITED BY H. W. WILEY.

Test for Carrot Color in Butter.—R. W. Moore, The Analyst, 11, 163. 10 gms. of the butter is dissolved in as little carbon disulphide as possible, and 20 c. c. 90 per cent alcohol added. The mixture is shaken and allowed to stand. The mixture forms two layers, one consisting of alcohol entirely colorless, the other of carbon disulphide containing all the color. On adding a drop of a dilute solution of ferric chloride and shaking, a change gradually takes place, the alcohol absorbs the color and the carbon disulphide becomes colorless. Care must be taken not to add too much ferric chloride. *H.*

Preservation of Milk Samples for Reference.—A. H. Allen, The Analyst, 11, 203. The milk is poured into double its weight of methylated spirit. More or less coagulation takes place but the curd is so finely divided that it is easy to get an average sample. Specimens have been kept successfully in this way for six months. *H.*

The Estimation of Acetic Acid in Liquids Containing Organic Matter.—(H. W. Wiley, Chem. News, 54, 34.) The author has examined the method of Duclaux (Ann. d. chim. et. Phys. 5 XI, 233 et. seq.) with reference to the estimation of acetic and lactic acids in kumys, and obtains the following results.

1. The sample of sour milk is mixed with an equal volume of alcohol, the acid determined in the filtrate with $\frac{1}{100}$ NaOH, using phenolphthalein as indicator. The quantity found, to be taken at 95 per cent. of the amount present.

2. 100 c. c. of the sour milk are diluted to 130 c. c. with water and a distillate of 100 c. c. taken off. The acetic acid in this distillate is estimated (using $\frac{1}{100}$ or $\frac{1}{1000}$ alkali if necessary).

If less than 12 c. c. $\frac{1}{1000}$ NaOH, are required to neutralize the acid in the distillate, it can be assumed that not more than 10 per cent. of the acetic acid present has been distilled over. From the total acidity, however, must first be deducted that due to the lactic acid carried over mechanically. If 0.3 per cent. lactic acid be present it will be proper to deduct 6 c. c. $\frac{1}{1000}$ from the total used. If 40 c. c. $\frac{1}{1000}$ be required under the conditions above noted, then 18 per cent. of the acetic acid may be considered to have come over. If 70 c. c. $\frac{1}{1000}$ NaOH be required the acid distilled over should be estimated at 23 per cent. If 110 c. c. $\frac{1}{1000}$ NaOH be required, place the amount of acid distilled over at 27 per cent. If the distillate require 200 c. c. $\frac{1}{1000}$ NaOH, the quantity of acid distilled over can be taken at 31 per cent. For quantities intermediate among those given, allow for proportionate percentages in the distillate.

Frothing of the Sample during Distillation.—Whether the object of distillation be the estimation of acid or alcohol, the difficulty of preventing frothing of the sample is great. I found that an ordinary test-tube brush, placed in the neck of the flask, was a most excellent safety plug. The handle of the brush should be cut off so as not to interfere with the stopper. A thread tied to the stump of the handle and left hanging outside does not interfere with the stopper and is convenient for withdrawing the brush. The brush should be

at first pushed into the flask, and then, by means of the thread, pulled up into the throat. The bristles then all point downward in a convenient position to puncture the bubbles. For alcohol distillations nothing better than this need be used. In the case of acids, however, there may be some danger of the metal of the brush being attacked, and some other device must be used. I found a small fine sponge pulled into the throat of the flask by a thread, very efficient means of arresting the bubbles. Another excellent device is the use of a plug of fine asbestos fibre or of glass wool. In all these cases the amount of liquid which the plugs will absorb must be approximately known, and this additional quantity of water added to the contents of the flask. I also employed a small platinum cylinder, punctured with fine holes which was attached by a rubber stopper to the delivery tube. The simplest device of all is to use a flask with a side delivery tube. The neck of the flask should be largest at the top and have a small constriction just as it enters the bulb. A perforated platinum cone large enough to fill the neck is placed point down in it. The constriction prevents it from entering the bulb. In this way the bubbles are prevented from entering the delivery tube, and no correction is to be made for absorbed liquids."

H.

TOXICOLOGY.

EDITED BY V. C. VAUGHAN, M. D.

The Identity of Cadaverin and Pentamethylenediamin.—Ladenburg, *Ber. der deut. chem. Ges.*, 19, 2585, has shown that the pentamethylenediamin, recently studied by himself, and the cadaverin, obtained by Brieger from putrefying flesh, are identical. Brieger first obtained this substance from the cadaver and gave for it the formula, $C_6H_{14}N_2$. Later Brieger's assistant, Bocklisch, obtained the same substance by the putrefaction of the flesh of fish. From the study of its properties, Brieger was struck with its resemblance to pentamethylenediamin, and asked Ladenburg to compare the two. This comparison has led to the establishment of their identity.

Detection of Chloral Hydrate in Toxicological Investigations.—Dragendorff (*Chem. Ztg.* 20, 144) discards the

usual methods and proceeds as follows: The contents of the stomach are acidified with dilute sulphuric acid, mixed with 3 volumes of 90 per cent. alcohol, allowed to macerate for 24 hours, and filtered. The alcohol is allowed to evaporate spontaneously in a flat dish, and the watery fluid agitated with petroleum spirit, which removes fatty and other matters. After removal of the petroleum spirit, the chloral is extracted by shaking with ether. The ether is allowed to evaporate, and the residue is then tested by the usual reagents for chloral. —*Analyst.*

The Production of Chemical Ferments by Koch's Cholera Bacillus. — H. Bitter, *Archiv für Hygiene*, 5, 241, has made an important contribution to our knowledge of the action of bacteria in general and of the common bacillus in particular; inasmuch as he has shown that some of the well-known effects of certain microorganisms are due to chemical ferments produced by the organism, but whose continued activity is independent of the life of the germ. Many bacteria by their growth liquify gelatine and coagulate albumen. This action, Bitter has shown to be due to a peptonizing ferment. For the demonstration of this Koch's comma bacillus is especially suited, since the germ is destroyed at a temperature of 60°, while the peptonizing ferment produced by the bacillus remains unharmed. The experiment is detailed as follows: A sterilized meat-pepton preparation (100 c. c. meat extract, 1.0 gram pepton and 0.5 gram sodium chloride) was infected with Koch's vibrio and kept at 37°. After five days there was a luxuriant growth in this fluid, and from it a tube (1) of similar fluid was infected to be used as a control. Then the original fluid was kept on the water-bath at 60° for half an hour, and from this warmed fluid another tube (2) was infected for a second control, and finally two other tubes (3) were filled with 10 c. c. of the fluid which had been sterilized by being heated to 60°, and a 10 per cent. solution of gelatine. All pipettes and tubes were properly sterilized. These tubes were then kept at 37° with the following results:

After 24 hours, tube (1) was filled with bacteria. This showed that before the temperature was raised to 60° the germs possessed full vitality.

After many days, tube (2) remained free from any growth. This showed that a temperature of 60° had thoroughly destroyed all vitality in the bacteria.

After 24 hours, the temperature of the two tubes (3) was lowered to 0° and the contents remaining fluid showed that the gelatine had been converted into pepton, and no bacteria appearing showed that this conversion into pepton had been accomplished without the direct agency of the bacteria.

The experiments were frequently repeated with like results, and convinced the investigator that the bacteria produced a ferment which continued active after the organisms had been destroyed. It was also shown that this ferment, like similar chemical ferments, would convert an indefinite amount of gelatin or coagulated albumen into pepton. It was also demonstrated that this ferment was more active in alkaline than in acid solution, thus proving that it resembled pancreatin more than pepsin. This resemblance to pancreatin was further demonstrated by the fact that certain chemicals, such as sodium carbonate and sodium salicylate, in small amounts increased its activity.

That a diastatic ferment is also produced by the growth of the bacillus was indicated by the development of an acid in nutrient solutions containing starch paste in which the comma bacillus was placed. However, all attempts to isolate the diastatic ferment were unsuccessful. A temperature of 60° destroys or greatly decreases the activity of ptyalin, and this seems to be also true of the diastatic ferment produced by the comma bacillus. But the formation of an acid from the starch presupposes that the starch is first converted into a soluble form.

The Diphenylamine Test for Water in Milk.—Szilasi makes this test as follows: 1 c. c. of solution of diphenylamine sulphate is put into a small porcelain dish, and a few drops of the milk added. If the milk has been diluted with water contaminated with nitrates, a blue color will gradually appear. This test is distinct when the milk contains not more than 5 per cent. of well water.—*Report. Anal. Chemie.*

NOTES.

—The first number of the "JOURNAL OF ANALYTICAL CHEMISTRY" has been delayed in the printing. We hope to avoid this delay with future numbers.

—With the beginning of the twenty-sixth year the *Zeitschrift für analytische Chemie* will appear bi-monthly instead of quarterly, as heretofore and the price will be increased from 12 marks (\$3) to 15 marks (\$3.75).

—The Third Annual Meeting of the Association of Official Agricultural Chemists was held in the rooms of the Chemical Division of the Department of Agriculture at Washington, D. C., on August 26th and 27th. Papers were read by Dr. Wiley, President of the Association, Mr. Clifford Richardson, Secretary, and by Messrs. Edgar Richards, Dr. W. J. Gascoyne, Dr. Wm. Frear and H. B. McDonnell, Dr. H. C. White, Dr. Chas. W. Dabney and G. L. Spencer. The proceedings have been published in full as Bulletin No. 12, of the Department of Agriculture, Division of Chemistry, which can be had by addressing the Secretary, Mr. Clifford Richardson, Washington, D. C.

—It is strange how few chemists have any knowledge of glassblowing. Very many can scarcely make a sightly bend in a glass tube, much less make a test-tube or join one tube to another. This much knowledge is easily acquired and no one should be without it; the only thing needed is a little practice in training the eye and hand and an occasional 10 minutes spent in watching a good glassblower. A book upon this subject has lately appeared in England* which may be of assistance to those who have no opportunity to see a glassblower at work; usually, however, observation of some one else is the best way to learn.

* The methods of Glass-Blowing, by W. A. Shenstone, London: Rivingtons.

DETERMINATION OF ANTIMONY IN HARD LEAD BY MEANS OF SPECIFIC GRAVITY.

BY GEORGE FAUNCE.

IN preparing hard lead for the market, the writer has often felt the need of a quick and accurate method for determining the antimony in the metal. Determination by specific gravity was one of the plans thought of, and a series of investigations was carried on to test the accuracy of the method. A set of samples of known composition was prepared by melting together pure lead and antimony. The greatest care is essential in melting the ingredients, as antimony is very easily oxidized; and unless the mixture is melted under charcoal or in a reducing flame, the resulting sample will contain less than the calculated amount of antimony. It is also essential that the portion selected for determination should have no air bubbles.

A number of determinations were made on each sample, with due observance of all the usual precautions, as to temperature, etc. Annexed is a table of results; which, however, are not the absolute results obtained, but are taken by measurement from the curve which conforms most closely to the average of the observations.

From this table it is seen that, between pure lead and lead alloyed with 25 per cent. antimony, there is a decrease in specific gravity of about .07 for each additional per cent. of antimony, a difference easily perceptible even in a rough estimation. If care is taken in preparing the sample we may suppose this method to be accurate to one quarter of one per cent. The greatest drawback in this method is the liability of getting samples that are not perfectly homogeneous.

122 DETERMINATION OF ANTIMONY IN HARD LEAD.

STANDARD OF TEMP.=15°C.

<i>Per Cent. of Antimony</i>	<i>Spec. Gravity.</i>	<i>Per Cent. of Antimony</i>	<i>Spec. Gravity.</i>
Pure Lead	11.369	18	10.098
1	11.293	19	10.036
2	11.217	20	9.974
3	11.143	21	9.914
4	11.070	22	9.855
5	10.996	23	9.795
6	10.922	24	9.737
7	10.850	25	9.679
8	10.778	30	9.39
9	10.706	40	8.86
10	10.634	50	8.38
11	10.565	60	7.96
12	10.495	70	7.59
13	10.425	80	7.27
14	10.358	90	6.97
15	10.291	Pure Antimony	6.686
16	10.225		
17	10.161		

It must not be forgotten that commercial hard lead contains a certain amount of copper, which has a considerable affinity for antimony. By skimming the melted alloy as cool as possible, most of the copper may be removed in a dross which contains also a larger proportion of antimony than the clean metal. A certain amount of copper, however, always stays with the latter in proportions varying with the amount of antimony, and with the temperature at which the dross is taken off. In good clean lead it should not exceed 1 ½ per cent. for 25 per cent. of antimony.

Will not the presence of copper vitiate the results obtained? This question was tested in exactly the same way as the first, viz., by making up samples of the desired composition. The results show that small amounts of copper change the specific gravity so slightly that they may be neglected. For example an alloy of the composition, 79 parts lead, 20 parts antimony, and 1 part copper gave Sp. Gr.=9.981 ; where lead 80, antimony 20, gave Sp. Gr.=9.974, or a difference corresponding to only one-tenth of one per cent. of antimony.

It is interesting to note that the amount of the *difference* in specific gravity due to increased percentages of antimony diminishes as the antimony increases. For instance, the decrease in Sp. Gr. between one and ten per cent. antimony is .735; while between ninety and one hundred per cent. antimony the decrease is only .284. For this reason, if for no other, the method is not a good one for alloys containing very large percentages of antimony.

NOTE ON SOXHLET'S AREOMETRIC METHOD OF ESTIMATING FAT IN MILK.¹

BY H. W. WILEY.

Caldwell and Parr² call attention to the difficulty which is often experienced in using Soxhlet's areometric method for the estimation of fat in milk. They say, speaking of the determination of fat by the lactobutyrometer:—"but in this case, while the butyrometer gave tolerable results, Soxhlet's method failed entirely; even after standing five hours, the layer of ether fat solution in the mixing bottle, which should be over a centimetre thick, was hardly a millimetre thick."

This experience is so much in harmony with my own that I thought it would be of interest to call attention to some of the difficulties encountered in working with Soxhlet's method.

Soxhlet's original paper was published in "*Zeitschrift des Landwirthschaftlichen Vereins in Bayern*" in 1880.

It rests upon the assumption that an alkaline milk shaken with ether will give all its fat to the ether, and this solution, being lighter than the rest of the mixture, will collect at the top, where it can be separated and its specific gravity determined.

The reagents used are ether saturated with water and a solution of caustic potash containing 400 grams to the litre.

The milk and reagents having been brought to a temperature of 17.5° are measured into a flask, (I use an ordinary pint beer bottle), with pipettes furnished with the apparatus. 200 c. c. milk, 10 c. c. of potash solution and 60 c. c. of the aqueous ether are the quantities to be employed. The milk is first placed in the flask and to this the potash solution added and shaken vigorously. Afterwards the ether is added and

¹ Read at the Meeting of the American Association for the Advancement of Science, Buffalo, Aug., 1886; communicated by the author.

² *Am. Chem. Journal*, 7, 245.

the shaking continued for one minute longer. The bottle is then put into water at a temperature of 17.5° and gently struck on the table in a vertical position at intervals of half a minute for fifteen or twenty minutes. At the end of this time the ether-fat solution has collected at the top, whence it is passed to the areometric cylinder by means of the rubber bulb blowing apparatus shown in the figure.

Water is now added at a temperature of 16° — 18° to the outer cylinder and after the temperature has become constant the density of the ethereal solution is read on the scale of the areometer. At the same time the temperature is read from the delicate thermometer attached to the areometer. The areometric degree is to be increased or diminished by the difference between the observed temperature and 17.5° as the former is above or below the latter. The percentage of fat is taken from a table which gives the numbers representing it for all degrees of the Soxhlet's scale between 43 and 66 for whole milk, or 2.07 to 5.12 per cent.; and for skimmed milk from 21.1 to 43, or from 0.00 to 2.07 per cent. It is thus seen that the scale includes all percentages of fat from nothing to 5.12. If a milk contain more than the latter percentage of fat it must be treated with a certain proportion of water before it can be examined by the Soxhlet's method.

Both Soxhlet in his original paper and Liebermann¹ affirm that the ether retained in the form of an emulsion in the lower part of the liquid in the flask does not contain a trace of fat. It is, therefore, necessary to assume that the emulsion has always the same proportion of ether, otherwise there would be variations in the density of the clear supernatant solution. This may be entirely true with those milks which permit the ether solution to separate readily, but where the separation is difficult and a great deal of time is required for it to take place, it is possible that this assumption may not hold good.

Liebermann, who having once condemned Soxhlet's method on account of the slow separation of the ether solution, introduced a modification of gently shaking the mixture and then pronounced it successful. He says² "Therefore the manner of making the first shaking with ether is not immaterial. The shaking must not be violent, (Soxhlet says 'schütteln eine halb minute kräftig),' but nevertheless, always sufficiently so. The light vertical blows must also be skillfully applied. In fact these are things which can only be attained by the skilled touch coming from experience."

¹ Zeitschrift anal. Chem., 1884, p. 478.

² Zeitschrift loc. cit.

It appears from the above, and my own experience fully convinces me of the truth of it, that in order to secure a proper separation of the ether fat solution, in all cases, one must be possessed of the art of legerdemain.

After giving the preference to his own volumetric method Liebermann ends his paper by the remark: "but if on the contrary, the method of Soxhlet is employed, it will usually happen that a given milk must be examined twice, once to see whether the original method is applicable, and again, in case of failure, with the necessary modifications."

I think it will be readily agreed that such a method can find no place in the examination of the milk of individual cows for each sample of which a special modification of the method would have to be made.

Schmøger¹ calls attention to the shortcomings of Soxhlet's method when milk poor in fat or skimmed milk is used. He says milk containing under 2 per cent. of fat must be evaporated with gypsum before it will give up its fat to ether. Yet it must not be forgotten that gypsum will give up something to ether, also. Schmøger obtained from 20 grams of pure ignited gypsum 5 mg. and from 20 grams sea sand 2 mg. of extract. These facts must be taken into consideration when the gravimetric comparisons of fat per cents with the areometric results are made. Certain variations in the method of making these gravimetric determinations have lately come into use, which promise some improvement. Babcock² substitutes ignited asbestos for sand or gypsum. This, in my opinion, is a great improvement. Babcock³ also dispenses with the evaporating dish and uses a tube open at both ends filled with asbestos, with a plug of cotton at each end. The milk is absorbed by the asbestos, the tube is then placed in a steam bath and a slow current of air drawn through it by an aspirator. In two hours the desiccation is complete. The method gives satisfactory results. It is inconvenient, however, to work a large number of samples at once by this method. After dry-

1. Bericht ueber die Thatigkeit des Milchwirthschaftlichen Instituts zu Proskau, as quoted in Zeitschrift anal. Chem. 1885, p. 130.

2. New York Ex. Sta. Report, 1883, p. 167.

3. loc. cit.

ing, the tube is placed in a continuous extractor and the fat removed by ether. I have used the following modification of the gravimetric method. The evaporation is made in a Schälchen half-filled with fine, pure asbestos. About 5 grams of milk are taken for each determination. The water is driven off at 100° and after the total solids have been noted by weighing, the asbestos is removed to the extraction tube. The Schälchen is then, finally, ground in a mortar, transferred to the extraction tube and the mortar and pestle thoroughly washed with ether. The extraction is then made in the usual way.

Adams¹ proposes the use of blotting paper rolled into a helical coil as the absorbent of the milk for the purpose of drying and extraction of the fat. Johnstone² modifies this method by using discs of blotting paper held in a circular platinum dish. Dr. Vieth³ hesitates to approve the blotting paper method on account of the fact that blotting paper itself gives up a considerable extract to ether.

Allen and Chattway⁴ recommend certain modifications in Adams' method consisting in a peculiar method of winding the coil of blotting paper.

Thompson⁵ proposes the use of filtering paper instead of blotting paper. I have had this method tried in my laboratory by Mr. Knorr and with pleasing results. Care must be taken, however, to use only filtering paper which has been previously thoroughly extracted. It was found that the filtering paper necessary to absorb 5 grams of milk was afforded by a piece 24 in. in length by 2.5 in. in breadth. This paper extracted with ether gave the follow residues :

No. 1	11.4 mg.
No. 2	13.4 "
No. 3	12.0 "
No. 4	10.5 "
No. 6	12.2 "
No. 7	20.9 "
No. 8	15.5 "

1. Analyst, 1885, p. 48.

2. op. cit. 1885, p. 83.

3. op. cit. 1885, p. 86.

4. Analyst, April 1886, p. 71.

5. Analyst, April 1886, p. 73.

The paper method has been adopted by the English Society of Public Analysts.¹ The English analysts admit that by the Adams' method at least .2 per cent. more fat is extracted than by any of the older methods of first evaporating the milk in sand or gypsum.

Since the tables of the Soxhlet method are based on the old method of extraction they will have to be revised for the new data given by the Adams' method.

One great advantage of the Adams' method as modified by Thompson I have found to consist in the rapidity with which the preliminary drying is accomplished. I have been able to put 5 c. c. of milk on a strip of paper, hang it over a sand bath and have it rolled and in the extractor within five minutes. I use an ingenious modification of Soxhlet's syphon extractor made by Mr. A. E. Knorr.

I mention this to show that even in the matter of gravimetric determinations by which the areometric method is finally judged, there is still a certain limit of variability.

I will return now to the subject more immediately under discussion. Schmöeger further says² that with skimmed milk, butter-milk, and such milks as have stood 24 hours on ice the ether-fat solution separates difficultly or not at all. To avoid this he recommends, after the addition of the potash, fully 5 minutes shaking, in order to form butter of the fat. Then the ether is added and the process continued as usual. In this case the percentage obtained by the areometric method must be increased .1 per cent. in order to agree with the gravimetric determinations. Schmöeger further recommends that skimmed milk or sweet butter-milk after treatment with potash be shaken with 10 grams potassium sulphate until the latter is dissolved. But this method also influences the specific gravity of the ether-fat solution and the corrections to be made are found in the table given.³

Soxhlet himself⁴ has called attention to the fact that with

1. Analyst, January, 1886, pp. 3-11.

2. loc. cit.

3. Ibid. p. 132.

4. Zeit. d. land. Ver. in Bayern, 1882, p. 18.

skimmed milk the ether-fat solution does not readily separate. A special scale has been constructed for such fat-poor milks giving areometric readings from 21.1 to 43, with the corresponding percentages of fat. For such milks Soxhlet proposes the following treatment, viz., a soap solution is made by taking 15 grams of a stearine candle, adding to it 25 c. c. alcohol, and 10 c. c. of the potash solution of the strength before given. The stearine is saponified by heating the mixture, and after the solution has become clear it is made up to 100 c. c. with water. From .4 to .5 c. c. of this solution is added to the milk under examination and after a good shaking the rest of the process is carried on in the usual way. After the first thorough shaking on the addition of the ether the light jolting must be continued for fifteen minutes at intervals of half a minute in order to have the ether solution collect at the top. At longest, the solution separated after 3 or 4 hours.

Halenke and Möslinger¹ call attention to the fact that if samples of milk are kept for some time even on ice, the ether-fat solution will no longer separate. They prefer in such cases, a modification of Liebermann's method, which they describe. In general I may say the areometric method has met with the approval of all analysts who have used it with exception of Preusse² but Soxhlet³ has shown that Preusse did not understand how to use the apparatus.

The following chemists, in addition to those already mentioned, have given the method their entire approval: Egger, Kellner, Schrodtt, Friedländer, Meissel, Fleischman, Hofmeister, Deitzell, Moser, Schreiner, Janke, Gerner and Angström.

I will give now some of my own experiences with the areometric method:

The milk examined by me was mostly obtained from a neighboring dairy and was a mixture from forty cows. Samples were also got of dealers in the city. The milk from the dairy mentioned was drawn at 5 P. M., and the examination made the following morning. This may partially account for

1. Ber. Bay. Vertreter der angewand. Chemie, 1885, p. 110.

2. Mittheil. Reichsgesundheitsamt, Vol. 1, p. 378.

3. Zeit. d. landw. Ver. in. Bayern, 1881, p. 700.

the small success I had in securing a good separation of the ether-fat. The work extended from March 23 to May 7, 1886.

With the first series of samples, in which the method of separation recommended by Soxhlet was followed, ninety-three trials were made. In only four cases was the separation sufficiently good to get a reading within 30 minutes. A larger number of readings was obtained within an hour, and about half the number could be read at the end of 3 or 4 hours. Of the remainder about one half could be read after 24 hours, and the rest did not separate at all. The results of reading the areometer at different times, however, showed that the density of the ether-fat solution underwent quite a change. The following data will show the nature and extent of this change :

No.	First Results.	Results after 24 Hours.	Difference.
1.	4.16 per ct. fat	4.08 per cent.	—0.08
2.	3.52 " "	3.83 " "	0.31
3.	3.20 " "	3.52 " "	0.30
4.	3.63 " "	3.68 " "	0.05
5.	5.28 " "	5.28 " "	0.00
6.	4.81 " "	5.13 " "	0.32
7.	4.81 " "	4.71 " "	—0.10

From the above it is seen that there is no uniformity in the character of this change, but in the greater number of cases the areometer shows an increase in the percentage of fat on standing.

Attempts also to obtain a more perfect separation by varying the quantity of potash employed gave only conflicting results.

I was, therefore, forced to the conclusion that for general work, Soxhlet's method would prove useless unless some method could be devised to secure a prompt and uniform separation of the ether-fat solution.

Various theories have been proposed to account for this peculiarity of milk in refusing to allow the ether solution to separate. Caldwell and Parr have supposed it to be due to the bran in the cow's food; Liebermann ascribes it to failure

of manipulation ; Schmöger that it is caused by the milk standing on ice; Soxhlet thinks it is the result of deficiency of fat; and others attribute it to differences in age and breed of the cows. The resumé which precedes shows that not only the actual volume of the ethereal solution but also the time of the separation required, has a serious disturbing influence on the specific gravity of the ether-fat solution.

Therefore, the method, in order to be of general application, must be subjected to some radical modification.

In this direction were the attempts to secure a more prompt separation by varying the amounts of caustic potash solution employed. These attempts, as the record has shown, were entirely unsuccessful. Even if the different kinds of milk would permit a prompt separation by varying the quantities of alkali employed, the amount for each sample could only be determined by numerous and tedious experiments.

I, therefore, turned my attention in another direction. It seemed to me that a centrifugal machine might be used to secure this separation, and accordingly I had a cast-away drug-mill formerly used in the laboratory, modified so as to serve for this purpose. The machine was so arranged as to hold 4 separatory flasks and impart to them a high speed of rotation. The form of the machine, with modifications made is shown in the figure.

At this point of my investigations this apparatus was finished and I immediately subjected it to a trial.

Four samples which had not separated at all at the end of 3 hours, were placed in the apparatus and whirled for ten minutes. At the end of this time three of them had completely separated, and the fourth nearly so. The apparatus was set in motion again for five minutes, at the end of which time the separation of the fourth sample was accomplished.

The number of revolutions per minute of the machine was about 350.

It will be seen from the above that the very first trial of the machine was completely successful, securing a perfect separation of the ether-fat solution in a few moments in samples

which previous trial, by the usual method, had failed to separate in several hours.

The next determinations were made on a sample of milk purchased at the Department restaurant.

Duplicate flasks were treated in the usual way to secure the separation and only at the end of 2½ hours was enough clear solution obtained to get a reading :

No. 1 gave 2.40 per cent. fat.

No. 2 gave 2.30 per cent. fat.

The first set of samples of the same milk separated by the centrifugal, gave the percentages below:

No. 1 gave 2.52 per cent.

No. 2 gave 2.32 per cent.

The separation took place perfectly in ten minutes with a rate of revolution of about 300 per minute.

The second set of four samples was treated in the same way and separated completely in eight minutes. The following readings were obtained:

No. 1 gave 2.36 per cent. fat.

No. 2 gave 2.34 per cent. fat.

No. 3 gave 2.31 per cent. fat.

No. 4 gave 2.30 per cent. fat.

The third set of samples separated by the centrifugal showed the following percentages:

No. 1 gave 2.23 per cent. fat.

No. 2 gave 2.30 per cent. fat.

The volume of the clear ether-fat solution in each case was about 40 c. c.

The next trial was with milk also purchased in the Department restaurant. It proved to be one of the rare cases in which a reasonably prompt separation was secured by the old method. After 30 minutes about 25 c. c. of the ether solution

had separated which was enough to get a reading. Duplicate determinations were made:

No. 1 gave 2.08 per cent. fat.

No. 2 gave 2.04 per cent. fat.

Four separations of the same milk were also made with the centrifugal. Separation took place promptly in eight minutes at a speed of about 300 revolutions per minute, and the volume of ether-fat in each case was about 40 c. c.

No. 1 gave 2.01 per cent. fat.

No. 2 gave 2.01 per cent. fat.

No. 3 gave 2.00 per cent. fat.

No. 4 gave 2.04 per cent. fat.

Which is an agreement as close as anyone could expect.

Having thus shown that the centrifugal method was capable of making the areometric method applicable to almost every sample of milk I undertook a new series of experiments. In all 155 samples were subjected to treatment.

Of the 155 samples examined only 57 gave a good separation by the Soxhlet method in 30 minutes. Of the remaining 98, about half did not separate at all so as to permit a reading, and the other half only after several hours. Compare this with the centrifugal method, in which only 6 samples out of the whole lot required over 15 minutes for separation and only one was abandoned as entirely inseparable, and the more general application of the process is at once apparent.

Of the six samples mentioned above, three were from the same cow, a grade Short-Horn, 4 years old, weight about 800 pounds, in milk since July 1885. She gave 6 quarts of milk a day, was milked at 5 A. M. and 5 P. M. The samples of milk sent were taken at 5 P. M., on April 13th, 17th and 23rd respectively. The food received by this cow was the same as for all the others (36) from which samples were taken for analysis. They received at 5 A. M., 3 pounds of wheat bran, and the same of hominy chops, and then as much corn (maize) fodder as they could eat. The bran and chops were fed dry. In pleasant weather the cows were out until 3 P. M. They

were then fed ten pounds each of unthreshed oats. At 5 P. M. they got a half peck of chopped turnips and a repetition of the morning's feed of bran and chops.

The hominy chops used, showed, on analysis, the following composition:

Water	7.13 per cent.
Ash	2.53 "
Ether Extract	9.03 "
Carbohydrates	69.32 "
Crude Fibre.	2.36 "
Albuminoids	9.63 "

Two of the other samples were received April 27th and 30th from a thoroughbred Jersey, 4 years old, weight about 600 pounds, in milk since July 1, 1885, giving at the time about 5 quarts daily. On the 29th of April samples of milk were also treated from the same cow, but after dilution the centrifugal separation, although more than usually difficult, did not require so long a time as on the occasion mentioned.

There is nothing shown by the analysis, by the breed of cow nor by the food which gives any definite idea of the cause of the peculiarity in these milks, which does not permit a speedy separation. It certainly is not the quantity of fat present, for other milks having the same, more or less amounts of fat, separated without difficulty. In the absence of any further evidence on this point we can only attribute the phenomenon to bovine idiosyncrasy.

In all 90 samples were compared by the usual method of separation and by the centrifugal. By the former method the mean percentage of fat obtained was 4.01 and by the latter 3.88. It thus appears that the numbers obtained by the centrifugal method must be increased by .13 in order to correspond to those of the old method. This discrepancy is readily explained when it is remembered that by the centrifugal motion the percentage of ether left in emulsion would naturally be less than with the former process of separation. The ether-fat solution thus becomes more dilute and consequently has a lower specific gravity. When, therefore, the percentage of

fat in a milk determined areometrically, is calculated by the tables given for the old method of separation, it should be increased by .13 in order to represent the actual quantity present.

I think it safe to conclude from the data which have been obtained : first, that the method of Soxhlet cannot be applied to the determination of fat in American milks, especially if they be from individual animals. It works somewhat better on mixed milks from a large dairy, but even in this case it is a rare thing to secure a prompt separation and in most cases the method would be very difficult of application.

Second, that by the use of the centrifugal machine described, a prompt separation of the ether-fat solution can be obtained in all cases, even in those in which after 48 hours no separation whatever takes place by the usual method.

Third, that the estimation of the fat in milk by Soxhlet's areometer can only be accurately secured when standard volumes of aqueous ether and caustic potash are employed, when the volume of the ether-fat solution separated is sensibly constant and the time employed in separation sensibly the same. These conditions can only be secured by the use of the centrifugal machine described.

I propose to use a centrifugal apparatus also for assisting in the separation of the ether-fat solution in the lactobutyrometer; and it has already proved its usefulness in separating precipitates which subside very slowly.

I am of the opinion that such a machine would prove of great value in every chemical laboratory aside from its utility in determining the fats in milk.

ESTIMATION OF PHOSPHORUS IN IRON AND STEEL.

By E. F. Wood.

OF the methods of determining phosphorus in iron and steel, only two are worthy of consideration; these are, the acetate or citric acid method; which, while very accurate requires too much time and careful manipulation to be well suited for practical work, and the molybdate method originally worked out by Eggertz. This method is worked in two ways, the "Direct" in which the phospho-molybdate of ammonia is weighed as such (which will be treated of in this paper) and the "Molybdate Magnesia" in which the phosphoric acid contained in the phospho-molybdate is transformed into magnesia pyrophosphate, this latter procedure is unnecessary and undesirable; it requires much time and introduces new sources of error, as the magnesia pyrophosphate obtained in this way always contains molybdic acid and may contain oxide of iron unless great care is taken.

The direct molybdate method when properly worked is superior to the others in simplicity and time required, and fully equal to them in accuracy, and the two modifications worked out by the writer, further simplify the method and permit of very rapid work.

THE DIRECT MOLYBDATE METHOD, GENERALLY APPLICABLE TO IRON, STEEL AND MANGANESE-IRON ALLOYS.

METHOD A.

Weigh 1.63 gm. material into a 4 or 5 inch evaporating dish, add 35 c. c. 1.20 HNO_3 , cover with a watch glass, when violent action has ceased put over a lamp and boil down till nearly or quite dry, remove from lamp, and add 15–20 c. c. concentrated HCl , again boil down to dryness, and heat to 200°C for one hour or until there is no longer any smell of acid, remove from lamp, cool, add 30–35 c. c. concentrated

HCl, boil till all is dissolved except silica and graphite, dilute with a little hot water, filter into 200 c. c. beaker, washing filter with HCl and hot water. (The filtrate and washings need not exceed 125 c. c.) Boil down to 15 c. c., add 35-40 c. c. HNO_3 , Sp. Gr. 1.42, again boil down to 15 c. c., add 5 c. c. water, cool, add 70 c. c. molybdic acid solution, stir well, let stand at a temperature of 20° to 30° C for 2 hours, or until the yellow precipitate is completely settled and solution is perfectly clear. Prepare a weighed filter by drying a 6 or 7 cm. filter of Munktell's No. 1 Swedish paper for 35 minutes in steam drying bath at 100° C, weigh rapidly to within 1 milligram. Remove most of supernatant liquor with a siphon, filter remainder, and wash precipitate on to filter with water containing 2 per cent. of 1.20 nitric acid; wash precipitate and filter 4 to 6 times with this mixture, dry at 100° C. for 45 minutes (longer if precipitate is very heavy, the point of the filter should be blue when dried enough) weigh. The yellow phospho-molybdate of ammonia contains 1.63 per cent. phosphorus, so that each milligram=.001 per cent. phosphorus in sample.

METHOD B.

APPLICABLE TO STEEL AND WROUGHT IRON.

Weigh 1.63 gm. steel into 200 c. c. beaker, add 35 c. c. 1.20 HNO_3 and cover with watch glass, when violent action has ceased place over lamp and boil till carbonaceous matter is dissolved and solution is concentrated to 15 c. c., add 15 to 20 c. c. chromic acid solution, boil down to 15 c. c., add 5 c. c. water, cool, precipitate and weigh as in method A. For very rapid work nearly as accurate results can be obtained in one hour. When solution is concentrated after adding chromic acid solution, rinse into Erlenmeyer flask using as little water as possible (not over 8 c. c.), cool to 30° C., add 70 c. c. molybdic acid solution, previously warmed to 30° C., cork and shake violently for five minutes, let stand 10 minutes, when precipitation will be complete. Filter through weighed filter, wash, dry 15 minutes at 135° C. This method was tried in pig iron, but the concentrated HNO_3 precipitated silica in

such a form that it could not be filtered. This difficulty was avoided in

METHOD C.

APPLICABLE TO PIG IRONS.

Place 1.63 gm. in a 200 c. c. beaker, add 35 c. c. 1.20 HNO_3 , boil 3 or 4 minutes, add 3 to 5 drops hydrofluoric acid and 15 c. c. water, boil down to 15 c. c., add 18 c. c. chromic acid solution, boil 5 minutes. Filter through asbestos filter, wash filter with hot water, concentrate filtrate to 20 c. c., cool and precipitate. Time required about $2\frac{1}{2}$ hours. As yet satisfactory results have not been obtained on ferromanganese, though the method works well on white iron and spiegel up to 20 per cent. manganese (see test analyses).

SPECIAL REAGENTS, APPARATUS, ETC.

Molybdic Acid Solution.—To a mixture of 1200 c. c. water and 700 c. c. concentrated ammonia Sp. Gr. .88 to .90, add 1 pound (454 gm.) molybdic acid, stir till dissolved, add 300 c. c. 1.42 HNO_3 , cool, pour 700 c. c. of this solution into a mixture of 630 c. c. 1.42 HNO_3 and 1600 c. c. water, let stand 24 hours and filter as desired for use. A more strongly acid molybdic solution is undesirable as the precipitation of phospho-molybdate is slow and often incomplete. A solution much less acid is apt to deposit molybdic acid on standing.

Chromic Acid Solution.—Dissolve about 50 gms. CrO_3 in 1 liter 1.42 nitric acid, by warming. The solution should be renewed occasionally as it seems to lose oxydizing power on standing 3 or 4 weeks.

Filter Paper.—The best paper for filtering off silica and graphite in method A was found to be Schleicher and Schüll's No. 597, about 9 cm. diameter filter being used. For collecting and weighing the phospho-molybdate the most suitable paper found was J. C. Munktell's No. 1 Swedish. It was the lightest paper, lost less on treatment with acid liquids, filtered rapidly, and was close enough to retain the fine precipitate. Three $6\frac{1}{2}$ cm. filters each of Schleicher & Schüll's 597, 598 and 590 and Swedish were dried, weighed, treated with 50 c. c. each of acid filtrate from preceding estimations

of phosphorus, washed with dilute HNO_3 and water, dried and weighed again.

The average weight of

Schleicher & Schull's 598 papers	was	.4096 gm.	average less	.0023 gm.
"	"	597	"	"
"	"	590	"	"
Swedish	No. 1	"	"	"

Schleicher & Schüll's 589 was not close enough to retain the precipitate.

Schleicher & Schüll's 590 filtered rather more slowly than the Swedish and is much more expensive.

Asbestos.—The best grade of "long fiber asbestos" usually contains pieces of the mineral, extra long coarse fibers and other things which spoil a filter made of it, and are not easy to pick out. To clean, stir up about one-half pound of the best asbestos in a pail of warm water, (not necessarily distilled water) run the fingers through the mixture to catch and remove any extra long fibers. Let it settle for 2 minutes, then pour two thirds of this mixture into a coarse sieve, let the water drain off, press out the remaining water, dry and preserve for use. The remainder in the pail may be again treated with water and a further portion of good asbestos recovered.

To make a filter. Place in the bottom of a "carbon filtering tube" a small plug of glass wool, on top of this about $\frac{1}{2}$ cm. of dry asbestos, then pour in a thin mixture of asbestos and water till the filter is sufficiently close.

Evaporating Burners.—A very convenient burner is an ordinary Argand illuminating burner, mounted on an iron base, and provided with a sheet iron chimney about 10 cm. high. This burner gives a good heat better distributed than with a Bunsen burner, it is very easily regulated by the "switch" and will burn either gasoline gas or coal gas. When the flame just reaches the top of the chimney the temperature 3 cm. above the chimney is about 300°C .

For supporting the beakers during evaporation use a piece of asbestos millboard about 3 mm. thick, with holes cut slightly less in diameter, than the diameter of the beakers. This protects the sides of the beakers from direct heat and en-

ables the evaporation to be pushed more rapidly without drying nitrate of iron on the sides of the beakers above the level of the liquid, as will occur if an iron plate or sand bath is used.

EXPERIMENTS.

1. *To Determine Some Points in Regard to Solution of Metal.*—Results 1 and 2 by method A, 3 and 4 by the same, except that steel was added in portions to previously warmed HNO_3 , 5, 6 and 7, the steel was dissolved in warm aqua regia, 8 and 9 by method A, 10 by A, omitting the addition of HCl , 11 and 12 by solution in warm aqua regia, 13 and 14 by method A, 15 and 16 dissolved in warm aqua regia.

TABLE I.

<i>Anal. No.</i>	<i>Material.</i>	<i>Per Cent. Comb. C.</i>	<i>Per Cent. Silicon.</i>	<i>Per Cent. Phosphorus.</i>	<i>Avg'e Per Ct. Phos.</i>
1	Steel Rail No. 21	.60	.03	.149	.148
2	"	"	"	.147	
3	"	"	"	.144	
4	"	"	"	.148	
5	"	"	"	.149	.144
6	"	"	"	.143	
7	"	"	"	.141	
8	Car Wheel Iron	1.60	.88	.298	
9	"	"	"	.297	.298
10	"	"	"	.302	.302
11	"	"	"	.285	.285
12	"	"	"	.284	
13	Casting U.		3.17	.815	.819
14			"	.822	
15			"	.802	
16			"	.806	

Three results show that it is immaterial whether the steel is added to the acid or the acid to the steel—Nos. 1 to 4.

The results from dissolving in aqua regia are all low as has been found by Stöckmann (*Zeits. anal. Chemie*, **16**, 174) Fresenius (*Quan. Anal.*, 6th German Ed.) and others. The loss, sometimes small, is often quite appreciable (Results 11 and 12) and as nothing is gained by the use of aqua regia, it is well to wholly avoid it, and use only 1.20 HNO_3 for solution. The addition of HCl in method A is to insure all silica being rendered insoluble. If only HNO_3 is used, silica is apt to go into solution, and by separation as gelatinous silica later, to cause trouble. It has no influence on the final results, as experiments adding HCl immediately after the action of HNO_3 in

dissolving the metal that ceased, after evaporating dry, and its total omission gave identical results, not confirming Tamm's statement, (Chem. News, May, '84), that evaporating and igniting without HCl was necessary to secure all the phosphorus.

The HCl may be omitted with low silicon steel and should be with high manganese ferro, as the the solution of ferro froths badly when HCl is present.

2. *Interference with Precipitation of Phosphorus by Molybdic Acid Solution.*—It is well known that when steel is dissolved in HNO_3 and the phosphorus directly precipitated by molybdic acid, only a portion of the total phosphorus is obtained. This interference is commonly supposed to be due to the organic matter formed by the action of the HNO_3 on the combined carbon. It is destroyed by evaporation of the nitric acid solution, and ignition of the residue at a temperature of 300°C . Evaporation at 100°C . is not sufficient to destroy the interference (see table III) but strong oxydants, as chromic acid dissolved in 1.42 HNO_3 (see test analyses methods B and C), chlorate of potash and strong nitric acid, Prof. B. W. Cheever's method (Trans. Amer. Inst. M. Eng. 1884), or possibly hydrogen peroxide under certain conditions (table IV) destroy the interference. In table II samples of steel 7 and 21 were treated by method A, but evaporated and ignited $\frac{1}{4}$ hour, 1 hour and 2 hours respectively.

TABLE II.

<i>Anal. No.</i>	<i>Material.</i>	<i>Heated to 300 C.</i>	<i>Per Cent. Phosphorus.</i>	<i>Average Phos.</i>
17	Steel Rail No. 21	$\frac{1}{4}$ Hour	.143	.144
18		$\frac{1}{4}$ "	.144	
19		1 "	.149	
20		1 "	.147	
21	Steel No. 7	$\frac{1}{4}$ "	.127	.127
22		1 "	.129	.129
23		2 "	.131	.131

In table III the results marked D were obtained as follows: Dissolve 1 gm. of steel in 30 c. c. 1.20 HNO_3 , evaporate to dryness on steam bath at 100°C , moisten and dry till no smell of acid is perceptible, take up with 1.20 HNO_3 , filter, concentrate filtrate to 15 c. c., cool, then precipitate and weigh as

method A. The results marked E, were obtained by dissolving 1 gm. steel in 30 c. c. 1.20 HNO₃, boiling till carbonaceous residue was completely dissolved, and solution concentrated to 15 c. c. cooled, precipitated and weighed. With pig iron this was slightly varied, 1 gm. heated with 30 c. c. 1.20 acid, boiled 5 minutes, 20 c.c. water added, boiled 2 to 3 minutes, filtered, concentrated to 15 c. c. and precipitated. Results in table IV were obtained by dissolving 1 gm. steel in 30 c. c. 1.20 HNO₃, boiling to complete solution, adding 25 c. c. hydrogen peroxide, boiling down to 15 c. c., cooling and precipitating.

TABLE III.

<i>Anal. No.</i>	<i>Material.</i>		<i>Comb. Car.</i>	<i>Silic'n</i>	<i>Phos. A.</i>	<i>Phos. D.</i>	<i>Phos. E.</i>	<i>Phos. E. + ½ E</i>
24	Pig Iron	A	.18		.116	.096		
25	"	B	.28		.117	.096	.084	.126
26	"	C	.18		.127	.099	.083	.125
27	"	D	.70		.134	.113		
28	"	E	.72		.103	.089	.068	.102
29	"	F	.45		.100	.086	.062	.093
30	"	G	.40		.115	.101		
31	"	H	.20		.125	.109	.086	.129
32	"	I	.86		.117	.099		
33	"	J	.30		.113	.097	.076	.114
34	Bessemer Steel.	2	.08		.053	.045	.032	.048
35	Old Rail	21	.60	.030	.148	.113		
36	Bessemer Steel	1	.06	.004	.098		.065	.098
37	"	3	.10		.141		.096	.144
38	Clapp & Griffith Steel	4	.15	.014	.389		.245	.367
39	Bessemer Steel	5	.23		.093		.065	.097
40	"	6	.24		.132		.090	.135
41	"	7	.54		.128		.083	.125
42	Crucible Steel	8	.55	.270	.050		.035	.052
43	Blown Metal Bessemer	10	.05		.110		.075	.112
44	Old Rail	11	.16	.390	.131		.085	.127
45	"	12	.26		.263		.163	.244
46	"	14	.24		.204		.127	.191
47	Bessemer Steel	15	.55	.088	.114		.072	.108
48	"	16	.28	.046	.089		.059	.089
49	"	17	.38		.073		.051	.076
50	"	18	.28		.097		.067	.100
51	"	20	.07		.100		.068	.102
52	"	22	.20		.151		.102	.153
53	"	23	.34		.072		.049	.074
54	"	24	.08		.100		.067	.100
55	"	28	.09		.093		.064	.096
56	"	29	.08		.092		.060	.090
57	Steel Nail Plate	13	.09		.102		.068	.102
58	Steel Axle	25	.10		.069		.048	.072
59	Old Rail	30	.23	.200	.080		.055	.082
60	"	26	.22		.197		.131	.196
61	"	27	.30		.189		.134	.201
62	Bessemer Steel	31	.69		.085		.057	.085
63	"	32	.61		.102		.068	.102
64	Steel Casting	33	1.02		.118		.081	.121

TABLE IV.

Anal. No.	Material.	Wt. of Phosphomolybdate			Per Cent Phos.	Per Cent. Phos. by A.
		Total.	in 25 c.c. H ₂ O ₃	Dif.		
65	Steel No. 34	.232	.160	.072	.117	.123
66	"	.234	.162	.072	.117	.123
67	"	.223	.161	.062	.101	.123

It will be observed that the phosphorus obtained by method E, was very nearly $\frac{2}{3}$ of the total phosphorus. The results by E+50 per cent. of themselves, agreeing closely with determinations by A, except in analyses 25, 29, 38, 45, 46 and 61, and the percentage of loss was wholly independent of the amount of silicon and combined carbon in the material. This would indicate that the interference is due to the formation of a modification of phosphoric acid not precipitable by molybdic acid solution, or of a definite organic compound of phosphoric acid, not to simple presence of organic matter in the solution, especially as added phosphorus (in the form of di sodium phosphate) is wholly precipitated.

3. *Proper Concentration of the Solution in which the Phosphomolybdate is Precipitated.*—Samples of steel No. 21 were treated by method A, but concentrated to different degrees and precipitated.

TABLE V.

Anal. No.	Solution Concentrated to	Water Added.	Per cent. Phosphorus.	Average Phosphorus.
68	15 c. c.	None	151	149
69	15 "	"	148	
70	35 "	"	138	
71	35 "	"	137	138
72	15 "	8 c. c.	149	
73	15 "	8 "	147	
74	15 "	30 "	140	139
75	15 "	30 "	138	
76	15 "	50 "	136	
77	15 "	50 "	137	137

Showing that for 1.63 gm. metal the solution should not exceed 30 c. c. This agrees with the statement in Post's Chem. Tech. Anal. p. 206. Under 15 c. c. the solution is syrupy and the precipitate will contain iron.

4. *Temperature of Precipitation.*—The best temperature is 20° to 30° C. Below 20° C, the precipitation is slow and often

incomplete. At high temperature molybdic acid is precipitated under some conditions, and arsenic, if present, is precipitated as arseno-molybdate. At 20° to 30° no arseno-molybdate is precipitated unless arsenic is present in large quantities. Arsenic added (as arsenic acid) to a steel in quantities representing .02, .05 and .20 per cent. did not precipitate any arseno-molybdate. But with arsenic equivalent to .50 to 3.50 per cent. a small amount of arseno-molybdate was precipitated at 25° C.

5. *Composition of Ammonio-Phosphomolybdate.*—Though the per cent. of phosphorus in the phospho-molybdate obtained in different ways may vary, it is sensibly constant when obtained under uniform conditions as in the analysis of iron. It can be dried to a constant weight at 100°C, and even when dried at 175° C on watch glasses or in a crucible, or at 135° C on filter paper the variation in weight is slight.

TABLE VI.

1 gm. dried on watch glasses.

<i>Anal. No.</i>	<i>Temp.</i>	<i>Time.</i>	<i>Loss.</i>	<i>Condition Before Final Drying.</i>
78	100° C.	½ Hour	.0025	Air Dried.
79	"	1 "	.0030	"
80	125°-130°	¾ "	.0025	"
81	"	1 "	.0050	"
82	"	1½ "	.0065	"
83	150°-155°	¾ "	.0010	Dried at 100°.
84	"	1 "	.0020	"
85	"	1½ "	.0060	"
86	170°-175°	¾ "	.0020	Dried at 150°.
87	"	1½ "	.0030	"
88	low red heat	¾ "	.0590	Dried at 100°
89	"	¾ "	.0570	"
90	red heat	¾ "		Melted and partly volatilized.

TABLE VII.

Phospho-molybdate From Steel Anal. Dried on Filters at 100°.

<i>Anal. No.</i>	<i>Weight Fil. dried 35m.</i>	<i>Fil. and Pre. dried 45m.</i>	<i>Precipitate dried 45m.</i>	<i>Dried 65m. Total Loss.</i>	<i>Dried 2h. 5m. Total Loss.</i>	<i>Dried 18h. Total Loss.</i>
91	.1960	.3180	.122	.0002	.0020	.0060
92	.2140	.3470	.133	.0005	.0015	.0060
93	.1885	.3360	.147	.0000	.0020	.0050
94	.1833	.3305	.147	0000	.0014	.0050

TABLE VIII.

Phospho-molybdate From Precipitation of Standard Na₂HPO₄ Solution Dried on Fillers.

<i>Anal. No.</i>	<i>Temperature</i>	<i>No. c. c. Na₂HPO₄</i>	<i>Precipitate dried at 100°</i>	<i>Precip. dried at high temp. 15 min.</i>	<i>Difference</i>	<i>Dried 30m. Entire loss</i>
95	135° C.	10	.1135	.1130	.0005	.0015
96	135 "	20	.2270	.2270	.0000	.0025
97	135 "	20	.2270	.2260	.0010	.0040
98	155 "	10	.1135	.1110	.0025	
99	155 "	20	.2270	.2200	.0076	
100	155 "	30	.3405	.3360	.0035	} Ignited in Gooch filt. crucible.
101	low red heat.	10	.1135	.1100	.0035	
102	"	30	.3405	.3240	.0165	

Showing that the phospho-molybdate can be safely dried at 100° C. The loss on 2 hours drying being only 1 per cent. and on 18 hours less than 4 per cent. At 135° C the loss becomes sensible after 40 minutes drying. The results on ignition were too irregular to be trusted. Though Meinecke says (Chem. News, Jan. 1886) that the yellow precipitate can be ignited to a constant weight. Samples of the phospho-molybdate were analyzed as follows: 1 to 2 gm. was dissolved in dilute ammonia, the phosphoric acid precipitated with ammonia and magnesia mixture; after standing 12 hours the impure phosphate of magnesia was filtered off, dissolved in HCl, a few drops of citric acid added, and the phosphoric acid precipitated with ammonia and magnesia mixture. After 12 hours standing, filtered, washed with dilute ammonia, ignited and weighed as magnesia pyrophosphate. The filtrates collected separate from the washings were measured, and for each 54 c. c. .0010 gm. added to the Mg₃P₂O₇ to correct for solubility of precipitate. The samples were all dried at 100° C before analysis.

TABLE IX.

<i>Anal. No.</i>	<i>Source of Phospho-Molybdate.</i>	<i>Per Cent. Phosphorus.</i>
103	From Analysis of Steel.	1.656
104	From Analysis of Pig Iron Sample A.	1.636
105	From Analysis of Pig Iron Sample A.	1.654
106	From Analysis of Pig Iron Sample B.	1.635
107	Na ₂ HPO ₄ Solution and Molybdic Acid Solution.	1.702
108	" " " " "	1.705

Giving average of 1.64 for phospho-molybdate as obtained

in actual course of analyses, which agrees very closely with the commonly accepted 1.63 per cent.

TABLE X.
Test Analyses—Comparison of Methods A and B.

Anal. No.	Material.		Comb. Car.	Silic'n	Per Cent. Phosphorus.	
					Method B.	Method A.
109	Bessemer Steel.	1	.06	.004	.098	.098
110	"	2	.08		.052	.053
111	"	3	.10		.139	.142
112	Clapp & Griffith Steel	4	.15	.014	.391	.387
113	Bessemer Steel	5	.23		.092	.093
114	"	6	.24		.132	.132
115	"	7	.54		.128	.128
116	Crucible Steel	8	.55	.270	.049	.050
117	"	9	.88	.138	.017	.017
118	Blown Metal Bessemer	10	.05		.110	.109
119	Old Rail	11	.16	.390	.127	.134
120	"	12	.26		.267	.265
121	Nail Plate Steel	13	.09		.102	.106
122	Old Rail	14	.24		.204	.207
123	Bessemer Steel	15	.55	.088	.113	.116
124	"	16	.28	.046	.086	.088
125	"	17	.38		.075	.072
126	"	18	.28		.097	.097
127	Partly Blown Metal	19	1.10	.33	.108	.112
128	Bessemer Steel	20	.07		.100	.100
129	Old Rail	21	.60		.174	.179
130	Bessemer Steel	22	.20		.151	.152
131	"	23	.34		.072	.072
132	"	24	.08		.104	.098
133	Steel Axle	25	.10		.071	.068
134	Old Rail	26	.22		.200	.192
135	"	27	.30		.191	.187
169	Washed Metal A.	{	about		.022	.022
170	Washed Metal B.		3.50		.012	.011

Showing the combined carbon and silicon in the amounts usually found in steel do not interfere. The steels were selected with a wide range of composition to test this.

TABLE XI.
Comparison of Methods C and A.

<i>Anal. No.</i>	<i>Material.</i>		<i>Comb. Car.</i>	<i>Sili- con.</i>	<i>Phos. A.</i>	<i>Phos. C.</i>
136	Pig Iron	B	.28		.117	.115
137	"	C	.18		.127	.127
138	"	E	.72		.103	.098
139	"	F	.45		.100	.105
140	"	H	.20		.125	.122
141	"	J	.30		.113	.108
142	"	K	.12	2.17	.120	.119
143	"	L	.05	6.00	.111	.108
144	"	M	.12	1.93	.118	.115
145	"	N	.07	3.15	.028	.029
146	"	O	.64	2.73	.040	.039
147	"	P	.79	2.48	.049	.048
148	"	Q	—	2.80	.031	.031
149	"	R	.52	1.28	.053	.051
150	"	S	.63	2.05	.067	.064
151	"	T	.47	3.20	.078	.082
152	Casting	U	—	3.17	.819	.819
153	White Iron	V	3.50	.20	.084	.085
154	86 Per Ct. Ferro. Mang.	W	} about 6.50	.76	.296	.280
155	"	X		.26	.277	.253
156	High Mang. Pig, Mn 5 Per Cent.	Y	} White Iron	2.00	.139	.141
157	High Mang. Pig, Mn 1 Per Cent.	Z		1.40	.127	.127
171	18 Per Ct. Spiegel		ab't 4.50		.141	.139
172	75 Per Ct. Ferromang.		" 6.00		.268	{ .241 .241 .238
	"		"		.265	
	"		"			

The method worked well on pig iron up to 6.00 per cent. silicon and on white iron and spiegel but failed on ferroman- ganese.

TABLE XII.
Influence of Hydrofluoric Acid.

<i>Anal. No.</i>	<i>Material.</i>		<i>Silicon.</i>	<i>3 drops HF</i>	<i>6 dr. HF</i>	<i>10 drops. HF</i>	<i>Phosphorus. Method A</i>
158	Pig Iron	K.	2.17	.120	.120	.101	.120
159	"	L.	6.00	.105	.106	.111	.111
160	Steel	34	.05	.125	.129	.138	.124

Excess of hydrofluoric acid leads to error either in acting on the glass and forming insoluble fluorides as in 160 or in preventing the precipitation of all the phosphorus. Steel 34 treated (in platinum) by method C, and 3 c. c. HCl added did not give any precipitate of phospho-molybdate.

TABLE XIII.

Test Analyses Method A, and Acetate Method.

<i>Anal. No.</i>	<i>Material.</i>		<i>Per Cent. Phosphorus.</i>	
			<i>Method A.</i>	<i>Acetate Method.</i>
161	Pig Iron	A 2	.103	.103
162	"	B 2	.100	.099
163	"	C 2	.118	.122
164	Steel	35	.131	.132
165	"	36	.134	.141
166	"	37	.132	.137
167	Pig Iron	D 2	.241	.243
168	Steel	F	.053	.056

Excellent results have been obtained by Prof. B. W. Cheever (Trans. Amer. Inst. Mining Eng., 1885) volumetrically, reducing the phospho-molybdate in sulphuric acid solution with amalgamated zinc (thus avoiding the irregular results obtained when ordinary zinc is used) and titrating with potassium permanganate.

But I think more rapid work can be done by weighing. If a rapid weighing, short arm balance is used, and the drying bath placed near enough to the balance so that it can be reached without getting up, 25 filters can be weighed in 20 minutes, making 50 weighings in 40 minutes. It is doubtful if 25 samples of phosphomolybdate can be dissolved off the filters, reduced and titrated in that time.

A NEW VISCOMETER.*

By S. M. BABCOCK.

A few experiments made with artificial emulsions, about one year ago, seemed to show that the creaming and churning qualities of milk were largely dependent upon its viscosity, and several attempts were made to measure this property of milk. The apparatus used for these trials consisted of a pipette with small jet, and was similar in principle to the viscometers generally employed for testing oils. It was soon demonstrated that methods of this kind could not be applied to milk, as small particles of solid matter are invariably present which partially clog the opening of the pipette so that duplicate determinations with the same sample rarely give concordant results. Experiments were also made with mechanical devices, none of which were successful, till the apparatus described below was constructed.

The apparatus consists of a disc of metal supported in its axis by an elastic wire, the torsion of which causes the disc to oscillate when a motion of rotation is imparted to it. At the lower end of this axis is rigidly attached a hollow cylinder, open at both ends, which is immersed in the liquid to be tested. The damping effect which the liquids examined have upon the motion of the disc furnishes a most sensitive measure of their viscosities. The motion being quite slow, and its direction being frequently reversed, there is little tendency to the formation of currents, and external friction is reduced to that of the air and the viscosity of the wire. Moreover, small particles of solid matter have little influence, as there are no corners and no projecting points against which they impinge.

The arcs of oscillation of a body suspended in this way diminish in a geometrical series, the ration of which depends

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upon the relation between the moment of inertia of the suspended body, the coefficient of torsion of the wire and the resistance to which it is subjected.

For the purpose of determining the length of the arc of oscillation, a circular protractor is attached to the upper surface of the disc, and a pointer fixed to the frame of the apparatus, directly above but not in contact with the scale.

The scale is numbered on the inside of the graduation from 0 to 360° , and on the outside the numbering is continued to 720° so that any arc may be directly read up to two complete revolutions. The point of equilibrium is adjusted by turning the support to which the upper end of the wire is attached until the zero point is directly beneath the stationary index. The reading may be greatly facilitated by a suitable magnifying glass placed directly above the index.

The essential parts of the apparatus should be so proportioned that the time of oscillation between two successive turning points will not be less than twenty seconds, and when very close results are essential the time of oscillation should be a minute or more, in order that the readings may be taken with accuracy.

The general construction of the apparatus is shown in figure 1, in which A represents the suspended disc; B, the scale consisting of a card board protractor 8 inches in diameter, and divided to half degrees; C, the stationary index; D, a large bulls eye lens; E, the resistance cylinder; F., vessel containing the liquid tested; G, the suspending wire; H, attachment of the wire; I and K, frame which incloses and supports the apparatus.

The several parts have the following dimensions. The wire is of tempered steel 0.2 millimeter in diameter and 110 centimeters long. The disc is of lead 12.6 centimeters in diameter and about 0.5 cm. thick, mounted in the middle of a brass axis 15. cm. long, and weighs, with its axis and resistance cylinder 1150 gms. The moment of inertia of the disc with the resistance cylinder attached is about 2,000,000,000 mgr. mm² and its time of oscillation 35 seconds.

The resistance cylinder is made from a piece of brass tubing

6.4 cm. in diameter and 5 cm. long, and is supported by a stiff wire which is connected to the axis of the disc by a small set screw so that it may be readily removed for cleaning.

The liquid to be tested is placed in a beaker, or other suitable vessel, which should be large enough to allow at least two centimeters between its sides and the revolving cylinder. The same vessel with which the apparatus is calibrated should



Fig. 1.

be used in all cases. The revolving disc should be inclosed to protect it from currents of air, which have a decided influence upon the result.

In order to determine the retardation due to the resistance of any substance, an impulse is given to the disc, with the cylinder immersed in the liquid, and the reading of the scale at each successive turning point noted. Any length of arc may be taken, but the initial impulse should be the same in all cases and should correspond to that for which the instru-

ment is calibrated. An arc of large amplitude has an advantage, as it reduces the influence which errors of scale reading have upon the result. In the tests already made, the initial impulse has been given by turning the disc, in the direction which causes the numbers on the scale to diminish, through one complete revolution or 360° , the starting point is then 0 and the first reading gives the length of arc of the first oscillation. In order to start the disc exactly at the zero point without vibration, it is necessary to have a clamp by which it may be held in the proper position and instantly released. The difference in the scale reading at adjacent turning points, gives the length of the arc of oscillation. The ratios of damping with different solutions may be best compared by the logarithmic decrements of these arcs. Representing the amplitude of the m th swing by a , and that of the n th swing by b , the logarithmic decrement will be

$$\frac{\log. a - \log. b}{n - m}$$

The number corresponding to this logarithm will be the ratio of damping. Five or six swings are sufficient for this determination.

It is possible, by determining the necessary constants of the apparatus, to calculate from the diminution of the arcs of oscillation the amount of energy required to overcome the resistance which any liquid offers, but the mathematical considerations involved are too complicated for general use, and would lead to confusion in the results, if this were taken directly as a measure of viscosity. To avoid the necessity for this calculation the viscosity imparted to distilled water by pure cane sugar is taken for a standard of comparison, the apparatus being calibrated as follows: A number of solutions, each containing a known quantity of sugar, are prepared and the amount of damping which each of these produces is determined. A curve is then constructed in which ordinates represent the number of grams of sugar per litre, and abscissas the amount of damping. This curve is quite regular, so that few points are required for its construction, and when once

made furnishes a simple means for expressing the viscosity of any liquid within its range.

The amount of damping may be expressed in several ways, two or three of which are indicated below. The sum of m arcs of oscillation, or the length of the m th arc of oscillation, or the reading of the m th turning point may be taken for the abscissas, but these methods require that the starting point in all determinations be absolutely the same, and that the index be adjusted exactly at the zero point of the scale. These precautions are not necessary if the abscissas are made to correspond to the logarithmic decrements obtained with each solution, as these are not materially affected by slight changes in length of arc. Four place logarithms may be used and the logarithmic decrements found taken as whole numbers, for the construction of the curve. See fig. 2, which represents a curve of this kind on a much reduced scale.



Logarithmic Decrements.

Fig. 2.

Having constructed a curve in one of these ways the viscosity of any liquid, more viscous than water, may be referred directly to a solution of sugar of the same viscosity, in which the amount of sugar is known, and this expressed in grams per litre gives the viscosity, on the scale adopted.

The utmost care is necessary in adjusting the temperature of the liquid tested, as very slight changes have a marked influence on the viscosity, increasing it rapidly as the temperature falls. Twenty degrees C., has been adopted as a standard temperature, this being near the average temperature of the room where observations are made. If the temperature of the room varies more than one or two degrees from that selected for a standard, some arrangement for maintaining the temperature constant during the test is necessary. A wooden vessel containing a considerable quantity of water adjusted to the proper temperature, in which the beaker containing the liquid tested may be placed, answers for this purpose. If the substance under examination is one whose coefficient of change for temperature is known, any temperature may be taken, and a corresponding correction can be made.

It is evident that the sensitiveness of the apparatus may be increased or diminished to any desired degree, by changing the resistance cylinder for one larger or smaller, or by changing the wire for one having a different coefficient of torsion. It also has an advantage over other methods in being applicable for substances having a wider range of viscosity, and in giving results with different instruments which are strictly comparable.

In order to better illustrate the use of the apparatus, an example is given.

<i>Scale Reading, Degrees.</i>	<i>No. of Arc.</i>	<i>Arc of Oscilla- tion.</i>	<i>Logarithms of Arc.</i>
686.1 } 65.8 } 625.8 } 120.0 }	1	620.3	2.7926
577.2 } 163.7 } 538.0 } 199.0 }	3	505.8	2.7040
	5	413.5	2.6165
	7	339.0	2.5302

The arcs of oscillation given above are for the first, third, fifth and seventh arcs, the intermediate ones being omitted so as to avoid the use of the same scale reading twice. The logarithmic decrement derived from the first and seventh arc is

$$\frac{2.7926 - 2.5302}{6} = .0437.$$

and from the third and fifth

$$\frac{2.7040 - 2.6165}{2} = .0437.$$

The logarithmic decrements found by the two calculations should not differ more than 1 or 2 in the last figure. A greater difference would show a considerable error in scale reading, and the test should be repeated. Considering this decrement as a whole number, we find by referring to the curve given in fig. 2, that it represents a viscosity equivalent to a solution of sugar containing 330 grams to the litre. The viscosity is therefore 330.

A few substances, among which are the lighter mineral oils, are less viscous than distilled water. For such, the above scale of viscosity furnishes no expression. If it were possible to continue the curve of viscosity indefinitely in this direction, the viscosity of all fluids could be stated in the same terms. I have not succeeded in doing this, and it seems necessary to adopt an artificial scale for liquids less viscous than water. I have considered such viscosities as negative and directly proportional to the difference between the logarithmic decrement found for the substance, and that for water at 30° C., this being the zero point of the scale. For convenience, I have assumed that distilled water at 20° C. represents 100 degrees of viscosity, so that the logarithmic decrement due to the resistance of water divided by 100 gives the decrement for one negative degree.

In order to make this plain, the following example is given. With the viscometer which I have used the logarithmic decrement with distilled water at 20° C. is .0233. Deducting from this the logarithmic decrement caused by the resistance of the

air and wire which is .0043 gives the decrement due to water alone, viz., .0190 and this divided by 100 gives .00019, the decrement for each negative degree with the instrument used.

A sample of benzine gave a logarithmic decrement of .0147, its viscosity is therefore— $\frac{.0088-.0147}{.00019} = -45$. While this scale does not in any way correspond with that for liquids more viscous than water, I believe it will give concordant values with different instruments, and thus enable observers to compare results. It will, however, be advisable, so soon as absolute values are determined, to change these negative values to correspond to the positive scale.

Aside from the examination of milk and butter, for which this instrument has been chiefly used, it will, I trust, find many applications in other lines. It appears to be especially well adapted to the examination of oils. Only a few tests, with the lighter oils have as yet been made, but with these it indicates very slight differences. The addition of one per cent. of benzine to a given sample of head light oil is readily shown, the difference in the logarithmic decrements for these oils being more than 100, with the apparatus used. This difference could be largely increased by using a larger resistance. For the heavy oils a much smaller resistance would be necessary, and possibly a heavier disc and stiffer wire would be an advantage.

Adulterations in sugar may be detected by dissolving a known weight in water, and making the solution up to a litre. The viscosity of the solution should equal the number of grams of sugar taken, if it is pure. The coefficient of viscosity for glucose is considerably less than for cane sugar, so that a small quantity added to sugar may be shown, if 300 or 400 grams of sugar are taken for the test.

Since this report was published my attention has been called to the researches upon fluid friction by Coulomb, whose apparatus was in principle indentical with that described in this article. It is therefore only the form of the apparatus and the method of expressing results which are new.

NOTE ON OPIUM ANALYSIS.

BY C. A. CRAMPTON.

IN the last number of the Journal L. D. Godshall gives an analysis made by E. Luttgen of a sample of opium, comparing the method given by Stillwell¹ with a modification of the method of the U. S. Ph. The per cents. show a very close agreement between the results by the two different methods.

A short time ago I was requested by Dr. Wiley to determine the morphine in a sample of opium sent for examination by the Treasury Department and in looking up methods, Stillwell's article, which had just been published, attracted my attention and as it seemed to be both rational and explicit, I used it, adhering carefully to all the details. I obtained the following results: 7.06—7.30, average 7.18 per cent., at the same time Mr. A. E. Knorr, of the Chemical Division, made an independent determination on the same sample using the same method except that, not having the morphiated solutions at hand, he transferred and washed the precipitate with a small quantity of water, making it practically the same as Squibb's method. He also used a Gooch crucible instead of the paper filter:—(a very convenient modification by the way). His result was 9.19 per cent. At my request he washed his precipitate thoroughly with the morphiated spirit and water that I had used, again dried and weighed it, when the weight thus obtained gave the result 7.36 per cent. bringing it down very nearly to my result. I subsequently weighed out some pure morphia in a Gooch crucible and washed it with 50 c. c. each, of the morphiated spirit and water, dried at 100° and found no loss of weight.

It would seem that one or the other of the two methods is very faulty and I would like to see Stillwell's method further investigated by some one accustomed to making morphia determinations, especially as neither Stillwell nor Teschemacher, the originator of the method, have given any comparative results by it.

Laboratory U. S. Dept. Agriculture.

1. Am. Chem. Jour. 1886, p. 295. This Journal, 1, 109.

THE DECOMPOSITION OF BLAST FURNACE CINDER BY ACID.

BY J. E. MERION AND EDWARD HART.

IN 1884 W. W. Iles contributed a paper to the Chemical News, Vol. 50, p. 194, in which he states that chilled lead cinder is completely decomposed when treated with hydrochloric acid, the residue left behind after evaporation to dryness and resolution in acid, consisting entirely of silica. No test analyses are given and the method was not applied to iron blast furnace cinder. It occurred to us that if it could be proved that hydrochloric acid always decomposes chilled blast furnace cinder, no matter what its composition, the method would be of considerable advantage in shortening the time necessary to make an analysis.

The following account of work done will show how far this proof has been furnished :

TAKING THE SAMPLES.

The samples taken were obtained by thrusting a warm bar into the cinder car or into the stream of cinder as it runs from the notch and allowing it to cool rapidly in the air. If the bar is not warm the cinder will not adhere ; if it is too warm cooling takes place too slowly and the sample becomes more or less crystalline. The samples taken in this way are almost perfectly transparent and glassy. Since even a small fragment represents a perfect sample of the material, sampling in the ordinary way is entirely unnecessary. A small fragment can therefore be ground to fine powder in the agate mortar within ten minutes after taking it from the furnace.

In making the silica determinations we have adopted a plan devised by Mr. H. G. Seaman, of Catasauqua, Pa. Instead of evaporating in glass or porcelain the evaporation is conducted in the crucible in which the fusion was made. We have used for this purpose ordinary fusion crucibles 40 cm. high and 35 cm. diameter. After fusion with mixed carbonates some water is added to the contents of the crucible which is placed in an in-

clined position on a triangle and hydrochloric acid is then run in slowly from a pipette, lifting the cover a little to one side for the purpose. Great care must be taken to avoid loss by spattering; the crucible cover is then replaced and the crucible heated gently until the evolution of carbon dioxide ceases; the lid is then taken off rinsed into the crucible and the contents evaporated to dryness. This is best done by placing the lamp directly under the crucible and four to eight inches below it, raising and lowering the flame until the proper temperature is reached. The evaporation takes place rapidly and, with a little practice, can be regulated so as to avoid spattering.

In the samples which were merely evaporated with acid without previous fusion the evaporation was carried on in the same crucibles. Rather less time is required and there is less danger of loss by spattering, as less gas is given off when the acid is added.

Unless some care is taken to prevent it the cinder is apt to form lumps consisting of an inner portion of undecomposed cinder and an outer envelope of gelatinous silica. The best way to avoid this is to add a few drops of water to the ground cinder before adding the acid, stirring with a platinum wire until a thin paste is formed, and then running in the acid from a pipette, stirring constantly with the wire. If this wire is heated in an oxyhydrogen blowpipe a globule of platinum forms on the end which makes a very convenient pestle for breaking up any lumps which have formed.

We first made four determinations on a sample of cinder from the Glendon furnaces to satisfy ourselves that the method gave agreeing results and obtained the following figures:

(1)	39.93	Per Ct.	SiO ₂
(2)	40.12	"	"
(3)	40.06	"	"
(4)	40.05	"	"

These results were obtained by fusion with sodium carbonate and subsequent evaporation with hydrochloric acid.

It is well known that most cinder when cooled slowly can only be partly decomposed by treatment with acid. To illustrate this two samples were taken from a car on April 8, 1886.

One of them on a warm rod and the other broken from the lump after cooling on the dump. Analysis gave the following figures :

Sample cooled slowly.	{	Fused with Na ₂ CO ₃ and evaporated to dryness with HCl.	37.97	Per Ct. SiO ₂ .
		Evaporated with HCl without previous fusion	39.65	Per Ct. SiO ₂ .
Chilled sample.	{	Fused with Na ₂ CO ₃ . . .	38.57	Per Ct. SiO ₂ .
		Evaporated with HCl {	38.63 38.58	" " "

The sample taken from the block of cinder came from the outside and contains less silica than the chilled sample from the same car. The results show that this cinder when slowly cooled is not perfectly decomposed by acid and is decomposed perfectly when chilled.

THE TITANIC ACID IN CINDER.

Much of the iron ore used in this vicinity contains titanic acid most of which goes into the cinder. The question soon arose as to whether the silica obtained from such cinder contains titanic acid and to settle this question we obtained a sample of chilled cinder from the Durham furnace, known to contain about one per cent. of titanic acid, and determined the silica by both of the methods described above. The following results were obtained :

No.	Acid Method.	No.	Fusion Method.
1	40.04 per cent.	2	40.00 per cent.
3	40.02 "	5	39.73 "
4	40.09 "	6	39.91 "
7	39.98 "		
8	40.01 "		

The silica from No. 7 and from No. 5 and 6 united was separately tested for titanic acid as follows: The silica was fused with about 4 times the weight of sodium carbonate and dissolved in water; any titanic acid present forms sodium titanate which is insoluble, while sodium silicate dissolves. As no residue whatever was left in either case the silica is evidently free from titanic acid. In order that the silica shall always be free from titanic acid, it is, however, necessary to use a fairly large amount of hydrochloric acid after evaporation to

dryness, and to heat nearly to boiling for several minutes. Any titanitic acid present then goes into solution leaving the silica pure. In the above analyses from .2 to .5 gm. of cinder was used and the mass after evaporation to dryness was treated with 10 c. c. hydrochloric acid sp. gr. 1.12, the heating being kept up for about 2 minutes; the solution was then diluted with an equal bulk of water before filtering off the silica.

(*To be Continued.*)

NOTE ON THE RESOLUTION OF IGNITED ALUMINA.

BY EDWARD HART.

IN an article in Silliman's Journal for August, 1886, p. 116, Penfield and Harper make the following statement: "We have also observed that when Al_2O_3 is ignited over a ring burner till a constant weight is obtained, then over a blast lamp, there is a slight loss, amounting in the quantities which we have used in the above experiments to about .0010 grams. What this loss represents we are not able to say. Usually in practical work this error cannot be avoided, because it is necessary to dissolve the ignited Al_2O_3 to test for traces of SiO_2 or iron, *and it is almost impossible to dissolve Al_2O_3 which has been strongly ignited over a blast lamp.*"

The italics are mine.

It is quite easy to redissolve strongly ignited alumina, as follows: About 5-10 times the weight of powdered potassium disulphate is added to the crucible containing the ignited alumina and the crucible heated to such a temperature that when the lid is off SO_2 escapes, but when covered there is no loss of SO_2 . Under these conditions the alumina dissolves, more or less slowly according to the temperature at which it has been ignited and its fineness. Sometimes it is necessary to keep up the heating for 7 or 8 hours but usually a shorter time suffices. Even corundum can be completely dissolved in this way. I know that this fact has been observed by others and only mention it because it seems not to be well known.

NOTE ON PERCENTAGE COMPUTATION, WITH TABLE FOR PHOSPHORUS.

BY WM. ST. G. KENT.

IN quantitative analysis the method of computation varies with individual preferences: the following is a type, viz:

$$x = 100 \frac{w m}{W}, \text{ when,}$$

x = the percentage of W required.

W = the weight of the material analyzed.

$w m$ = the desired weight of the constituent: (w being the weight of a stable compound resulting from the analysis and m the weight of the constituent contained in a unit weight of the compound w .)

By making W constant, weights of w containing x in commensurable quantity form a series in arithmetical progression, and tables so constructed for compounds in daily use, based on a unit value for W , yield x for W of any weight on dividing the given percentage by such weight; thus for phosphorus weighed as pyro-phosphate of magnesia ($Mg_2P_2O_7$) where,

$$I = 100 \frac{w \times .27928}{I},$$

$w = .0358063$ and becomes the common difference of arithmetical progression for values 2, 3, 4, 5, etc., of x .

The additive constant for the following table is $.0000358063^*$ giving .001, .002, .003, .004, etc., equivalent percentage values up to 2.000 per cent., the arrangement being similar to the ordinary one for logarithms. To avoid repetition, the first two figures of the decimal weight (placed to the left of ten succeeding columns, each containing the three remaining figures of weight) are not inserted except on their first occurrence or at the opening of a page: in the line of figures next above

* In a more extended table, atomic weights 30.96, 23.94 and 15.96 (of P, Mg and O respectively) $w = .000035775$ would in all probability afford results of greater accuracy.

and to the right of these principal figures of weight, “—” (the Morse cipher character) is used to locate a change in the first significant figure of the decimal ; this signal of change replaces two naughts.

TABLE OF $\text{Mg}_3\text{P}_2\text{O}_7$ GIVING THE PERCENTAGE OF PHOSPHORUS IN ONE GRAMME OF MATERIAL ANALYZED.

Per Cent.	0	1	2	3	4	5	5	7	8	9
00	000	004	007	011	014	018	021	025	029	032
01	036	039	043	047	050	054	057	061	064	068
02	072	075	079	082	086	090	093	097	100	104
03	107	111	115	118	122	125	129	132	136	140
04	143	147	150	154	158	161	165	168	172	175
05	179	183	186	190	193	197	201	204	208	211
06	215	218	222	226	229	233	236	240	243	247
07	251	254	258	261	265	269	272	276	279	283
08	286	290	294	297	301	304	308	312	315	319
09	322	326	329	333	337	340	344	347	351	354
10	358	362	365	369	372	376	380	383	387	390
11	394	397	401	405	408	412	415	419	423	426
12	430	433	437	440	444	448	451	455	458	462
13	465	469	473	476	480	483	487	491	494	498
14	501	505	508	512	516	519	523	526	530	534
15	537	541	544	548	551	555	559	562	566	569
16	573	576	580	584	587	591	594	598	602	605
17	609	612	616	619	623	627	630	634	637	641
18	645	648	652	655	659	662	666	670	673	677
19	680	684	687	691	695	698	702	705	709	713
20	716	720	723	727	730	734	738	741	745	748
21	752	756	759	763	766	770	773	777	781	784
22	788	791	795	798	802	806	809	813	816	820
23	824	827	831	834	838	841	845	849	852	856
24	859	863	867	870	874	877	881	884	888	892

Per Cent.		0	1	2	3	4	5	5	7	8	9
25	00	895	899	902	906	909	913	917	920	924	927
26		931	935	938	942	945	949	952	956	960	963
27		967	970	974	978	981	985	988	992	995	999
28	01	003	006	010	013	017	020	024	028	031	035
29		038	042	046	049	053	056	060	063	067	071
30		074	078	081	085	089	092	096	099	103	106
31		110	114	117	121	124	128	131	135	139	142
32		146	149	153	157	160	164	167	171	174	178
33		182	185	189	192	196	200	203	207	210	214
34		217	221	225	228	232	235	239	242	246	250
35		253	257	260	264	268	271	275	278	282	285
36		289	293	296	300	303	307	311	314	318	321
37		325	328	332	336	339	343	346	350	353	357
38		361	364	368	371	375	379	382	386	389	393
39		396	400	404	407	411	414	418	422	425	429
40		432	436	439	443	447	450	454	457	461	464
41		468	472	475	479	482	486	490	493	497	500
42		504	507	511	515	518	522	525	529	533	536
43		540	543	547	550	554	558	561	565	568	572
44		575	579	583	586	590	593	597	601	604	608
45		611	615	618	622	626	629	633	636	640	644
46		647	651	654	658	661	665	669	672	676	679
47		683	686	690	694	697	701	704	708	712	715
48		719	722	726	729	733	737	740	744	747	751
49		755	758	762	765	769	772	776	780	783	787
50		790	794	797	801	805	808	812	815	819	823
51		826	830	833	837	840	844	848	851	855	858
52		862	866	869	873	876	880	883	887	891	894
53		898	901	905	908	912	916	919	923	926	930
54		934	937	941	944	948	951	955	959	962	966

TABLE FOR PHOSPHORUS.

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Per Cent.		0	1	2	3	4	5	5	7	8	9
55	01	969	973	977	980	984	987	991	994	998	—2
56	02	005	009	012	016	019	023	027	030	034	037
57		041	045	048	052	055	059	062	066	070	073
58		077	080	084	088	091	095	098	102	105	109
59		113	116	120	123	127	130	134	138	141	145
60		148	152	156	159	163	166	170	173	177	181
61		184	188	191	195	199	202	206	209	213	216
62		220	224	227	231	234	238	241	245	249	252
63		256	259	263	267	270	274	277	281	284	288
64		292	295	299	302	306	310	313	317	320	324
65		327	331	335	338	342	345	349	352	356	360
66		363	367	370	374	378	381	385	388	392	395
67		399	403	406	410	413	417	421	424	428	431
68		435	438	442	446	449	453	456	460	463	467
69		471	474	478	481	485	489	492	496	499	503
70		506	510	514	517	521	524	528	532	535	539
71		542	546	549	553	557	560	564	567	571	574
72		578	582	585	589	592	596	600	603	607	610
73		614	617	621	625	628	632	635	639	643	646
74		650	653	657	660	664	668	671	675	678	682
75		685	689	693	696	700	703	707	711	714	718
76		721	725	728	732	736	739	743	746	750	754
77		757	761	764	768	771	775	779	782	786	789
78		793	796	800	804	807	811	814	818	822	825
79		829	834	836	839	843	847	850	854	857	861
80		865	868	872	875	879	882	886	890	893	897
81		900	904	907	911	915	918	922	925	929	933
82		936	940	943	947	950	954	958	961	965	968
83		972	976	979	983	986	990	993	997	—1	—4
84	03	008	011	015	018	022	026	029	033	036	040

Per Cent.		0	1	2	3	4	5	6	7	8	9
85	03	044	047	051	054	058	061	065	069	072	076
86		079	083	087	090	094	097	101	104	108	112
87		115	119	122	126	129	133	137	140	144	147
88		151	155	158	162	165	169	172	176	180	183
89		187	190	194	198	201	205	208	212	215	219
90		223	226	230	233	237	240	244	248	251	255
91		258	262	266	269	273	276	280	283	287	291
92		294	298	301	305	309	312	316	319	323	326
93		330	334	337	341	344	348	351	355	359	362
94		366	369	373	377	380	384	387	391	394	398
95		402	405	409	412	416	420	423	427	430	434
96		437	441	445	448	452	455	459	462	466	470
97		473	477	480	484	488	491	495	498	502	505
98		509	513	516	520	523	527	531	534	538	541
99		545	548	552	556	559	563	566	570	573	577
1.00		581	584	588	591	595	599	602	606	609	613
01		616	620	624	627	631	634	638	642	645	649
02		652	656	659	663	667	670	674	677	681	684
03		688	692	695	699	702	706	710	713	717	720
04		724	727	731	735	738	742	745	749	753	756
05		760	763	767	770	774	778	781	785	788	792
06		795	799	803	806	810	813	817	821	824	828
07		831	835	838	842	846	849	853	856	860	864
08		867	871	874	878	881	885	889	892	896	899
09		903	906	910	914	917	921	924	928	932	935
10		939	942	946	949	953	957	960	964	967	971
11		975	978	982	986	989	992	996	—0	—3	—7
12	04	010	014	017	021	025	028	032	035	039	043
13		046	050	053	057	060	064	068	071	075	078
14		082	086	089	093	096	100	103	107	111	114

TABLE FOR PHOSPHORUS.

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Per Cent.		0	1	2	3	4	5	6	7	8	9
15	04	118	121	125	128	132	136	139	143	146	150
16		154	157	161	164	168	171	175	179	182	186
17		189	193	197	200	204	207	211	214	218	222
18		225	229	232	236	239	243	247	250	254	257
19		261	265	268	272	275	279	282	286	290	293
20		297	300	304	308	311	315	318	322	325	329
21		333	336	340	343	347	350	354	358	361	365
22		368	372	376	379	383	386	390	393	397	401
23		404	408	411	415	419	422	426	429	433	436
24		440	444	447	451	454	458	461	465	469	472
25		476	479	483	487	490	494	497	501	504	508
26		512	515	519	522	526	530	533	537	540	544
27		547	551	555	558	562	565	569	572	576	580
28		583	587	590	594	598	601	605	608	612	615
29		619	623	626	630	633	637	641	644	648	651
30		655	658	662	666	669	673	676	680	683	687
31		691	694	698	701	705	709	712	716	719	723
32		726	730	734	737	741	744	748	752	755	759
33		762	766	769	773	777	780	784	787	791	794
34		798	802	805	809	812	816	820	823	827	830
35		834	837	841	845	848	852	855	859	863	866
36		870	873	877	880	884	888	891	895	898	902
37		905	909	913	916	920	923	927	931	934	938
38		941	945	948	952	956	959	963	966	970	974
39		977	981	984	988	991	995	999	—2	—6	—9
40	05	013	016	020	024	027	031	034	038	042	045
41		049	052	056	059	063	067	070	074	077	081
42		085	088	092	095	099	102	106	110	113	117
43		120	124	127	131	135	138	142	145	149	153
44		156	160	163	167	170	174	178	181	185	188

Per Cent.		0	1	2	3	4	5	6	7	8	9
45	05	192	196	199	203	206	210	213	217	221	224
46		228	231	235	238	242	246	249	253	256	260
47		264	267	271	274	278	281	285	289	292	296
48		299	303	307	310	314	317	321	324	328	332
49		335	339	342	346	349	353	357	360	364	367
50		371	375	378	382	385	389	392	396	400	403
51		407	410	414	418	421	425	428	432	435	439
52		443	446	450	453	457	460	464	468	471	475
53		478	482	486	489	493	496	500	503	507	511
54		514	518	521	525	529	532	536	539	543	546
55		550	554	557	561	564	568	571	575	579	582
56		586	589	593	597	600	604	607	611	614	618
57		622	625	629	632	636	640	643	647	650	654
58		657	661	665	668	672	675	679	682	686	690
59		693	697	700	704	708	711	715	718	722	725
60		729	733	736	740	743	747	751	754	758	761
61		765	768	772	776	779	783	786	790	793	797
62		801	804	808	811	815	819	822	826	829	833
63		836	840	844	847	851	854	858	862	865	869
64		872	876	879	883	887	890	894	897	901	904
65		908	912	915	919	922	926	930	933	937	940
66		944	947	951	955	958	962	965	969	973	976
67		980	983	987	990	994	998	—1	—5	—8	—12
68	06	015	019	023	026	030	033	037	041	044	048
69		051	055	058	062	066	069	073	076	080	084
70		087	091	094	098	101	105	109	112	116	119
71		123	126	130	134	137	141	144	148	152	155
72		159	162	166	169	173	177	180	184	187	191
73		195	198	202	205	209	212	216	220	223	227
74		230	234	237	241	245	248	252	255	259	263

TABLE FOR PHOSPHORUS.

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Per Cent.		0	1	2	3	4	5	6	7	8	9
75	06	266	270	273	277	280	284	288	291	295	298
76		302	306	309	313	316	320	323	327	331	334
77		338	341	345	349	352	356	359	363	366	370
78		374	377	381	384	388	391	395	399	402	406
79		409	413	417	420	424	427	431	434	438	442
80		445	449	452	456	459	463	467	470	474	477
81		481	485	488	492	495	499	502	506	510	513
82		517	520	524	528	531	535	538	542	545	549
83		553	556	560	563	567	570	574	578	581	585
84		588	592	596	599	603	606	610	613	617	621
85		624	628	631	635	639	642	646	649	653	656
86		660	664	667	671	674	678	681	685	689	692
87		696	699	703	707	710	714	717	721	724	728
88		732	735	739	742	746	750	753	757	760	764
89		767	771	775	778	782	785	789	792	796	800
90		803	807	810	814	818	821	825	828	832	835
91		839	843	846	850	853	857	861	864	868	871
92		875	878	882	886	889	893	896	900	903	907
93		911	914	918	921	925	929	932	936	939	943
94		946	950	954	957	961	964	968	972	975	979
95		982	986	989	993	997	—0	—4	—7	011	014
96	07	018	022	025	029	032	036	040	043	047	050
97		054	057	061	065	068	072	075	079	083	086
98		090	093	097	100	104	108	111	115	118	122
99		125	129	133	136	140	143	147	151	154	158

SHORT TITLES OF CHEMICAL PERIODICALS CURRENT IN 1887.

BY H. CARRINGTON BOLTON.

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CONVERSION OF MANGANESE TO PERMANGANIC ACID.

BY BYRON W. CHEEVER.

CAN all of the manganese, in a nitric acid solution, be oxidized to permanganic acid by boiling with lead dioxide?

This question has often been discussed by chemists, and many, and varied answers have been given, based upon the results obtained by each experimenter.

For the purpose of testing this question more thoroughly than could be done by comparing colors, experiments were made which involved the analysis of some of the products, and tests of others.

The reagents used were freshly prepared lead dioxide free from manganese; nitric acid free from nitrous fumes; a nitric acid solution of steel—containing a known per cent. of manganese—free from organic matter; freshly prepared crystals of ammonio-ferrous sulphate; and standard potassium permanganate. The last two were compared each day, and fresh solutions prepared if necessary.

As these solutions were to be used for titrating the permanganic acid in a nitric acid solution, tests were made to determine what strength of acid could be used with a weak permanganate solution, without destroying its color. It was found that 5 c. c. of $\frac{1}{100}$ KMnO_4 diluted with 75 c. c. HNO_3 (1.07 sp. gr.) did not change color in the cold, within ten or fifteen minutes; most held the color much longer, a few faded very rapidly. It was also found that this strength of acid did not interfere in titrating with ammonio-ferrous sulphate.

Attention was next directed to the oxidation of the manganese in the nitric acid solution of steel; the published methods were examined and tried, and the following modification was finally adopted as giving the most uniform results.

The solution containing the manganese, was placed in a two ounce globe-shaped flask, brought to a boil, then removed from the flame and about 0.5 grm. PbO_2 added; the flask was then so placed that the heat could be raised gradually, till the solution boiled briskly, (which required about three minutes); it was then removed by wooden clamps and immediately cooled under the hydrant; when cold, the solution was filtered through asbestos, and the filtrate titrated with a centinormal solution of ammonio-ferrous sulphate—a slight excess being used—and the excess titrated back with centinormal potassium permanganate.

In conducting these experiments upon the process, about 0.1 mgrm. of manganese was used in each trial, which being a very small amount, and thereby tending to increase the error, tests were made to determine the maximum amount which might be used; this was found to be 0.5 mgrm.

The following table contains the average results of a number of determinations made with this object in view:

<i>Mgrms. of Mn Taken.</i>	<i>Mgrms. of Mn Oxi- dized to HMnO_4.</i>	<i>Per Cent. Oxi- dized.</i>
0.11	0.110	100.
0.10	0.104	95.
0.55	0.539	98.
0.55	0.533	97.
0.9	0.739	82.
1.5	1.188	79.
2.1	1.100	52.
3.	1.450	48.

Having completed the work on reagents and process, a series of experiments was then made to decide the main question, namely, is the per cent. of manganese oxidized to permanganic acid, constant, under identical conditions?

Consecutive tests were made from time to time by my assistants and myself, for the purpose of eliminating as far as possible, personal defects in manipulating, and reducing the errors to a minimum.

The following twenty consecutive tests represent as nearly as possible an average of the whole. For each test, 10 c. c.

of the steel solution were taken, which contained 0.1 mgrm of manganese ; eighteen of the twenty gave from 95. to 100 percent of the manganese oxidized to HMnO_4 , and two gave respectively 70 and 77 per cent.

Many modifications of the method were tried without diminishing the percentage of errors.

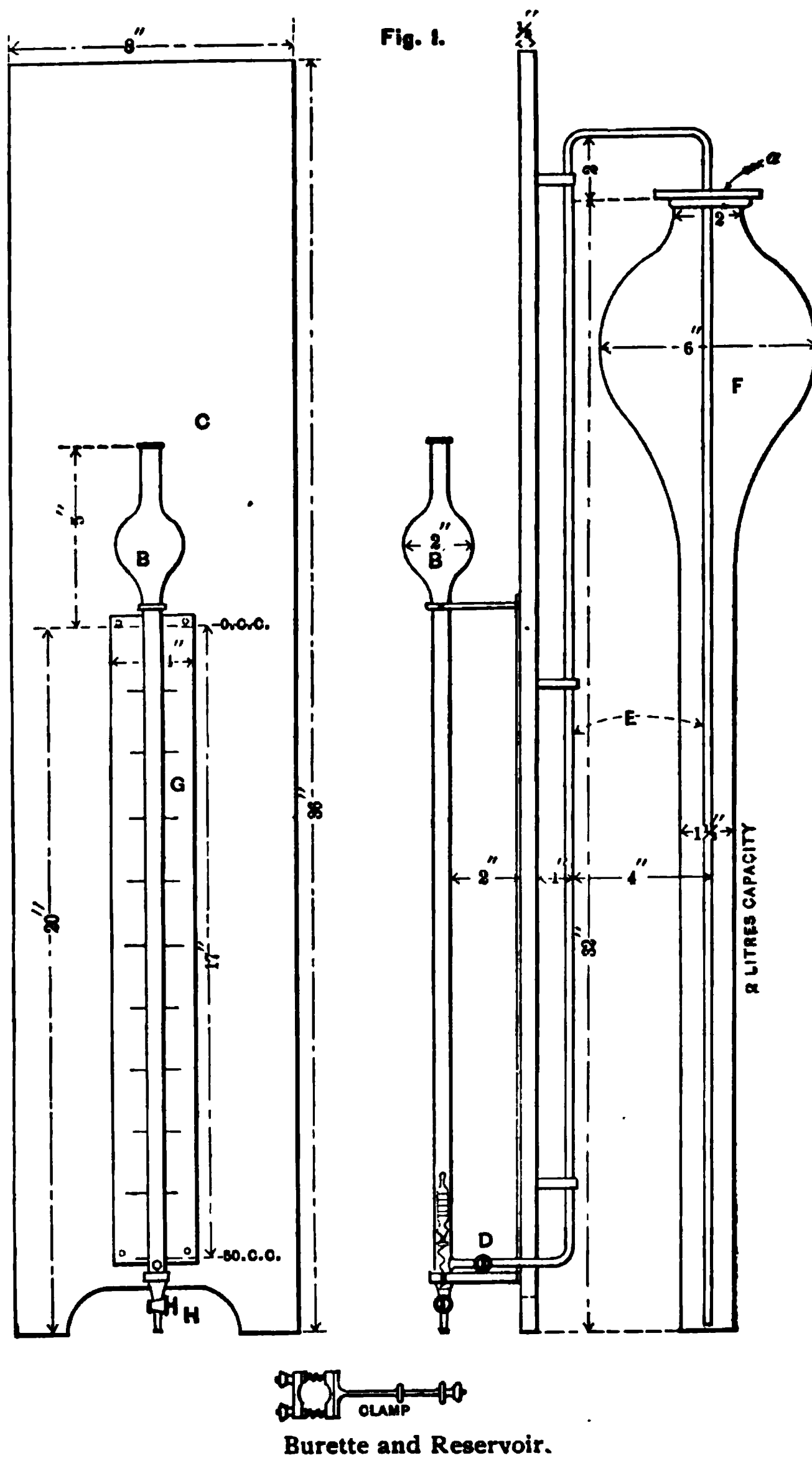
Where the per cent. of HMnO_4 was too low, the imperfectly oxidized manganese was found in one of three places, or in all three. First, in the filtrate with the HMnO_4 . Second, on the filter. Third, on the sides of the flask. In the last two cases it was without doubt in the form of MnO_2 .

ABSTRACTS.

APPARATUS AND REAGENTS.

Apparatus for Volumetric Determinations with Potassium Permanganate. — Clemens Jones. Read before the American Institute of Mining Engineers, Scranton meeting, Feb. 1887. "The burette B (50 c. c. to $\frac{1}{10}$ c. c.), shown in Fig. 1, consists of the graduated tube proper and an arm, E, fused to it below the 50 c. c. mark. At its top are rubber connections with the blast aspirator, shown in the cut (Fig. 2.) of the front view. By means of an extra stop-cock, D, connection through E is established with the reservoir F. The burette is clamped securely to a slide, C, which is counterpoised and moves freely on guides between two parallel sides, L, suitably mounted in a frame, and through their whole length. Back of the burette is a porcelain scale, G, graduated to correspond with it, and secured to the slide, in front of which the burette is adjusted. The reservoir, F, is suspended in a notched shelf within the frame, and is introduced through the side door, K, shown open in Fig. 2, and is then encased in a box which has an annular hole in the top to admit the prong of the tube E. It is so placed that when the slide is at the lowest point the inlet-prong has a safe margin from the bottom. A round glass plate, *a*, ground to fit the top of the reservoir, receives the inlet-prong through a hole in the center.

Either float or meniscus can be used in reading. The writer gives preference to an Erdmann float, having two stripes of white paper pasted inside, equidistant from the etched line and half an inch apart. No difficulty is experienced in reading with this to .06 c. c., or even .01 c. c. The float remains in the burette permanently, and is caught on a stage of fine



platinum wire supported by a spiral, when it descends within half an inch of the inlet tube.

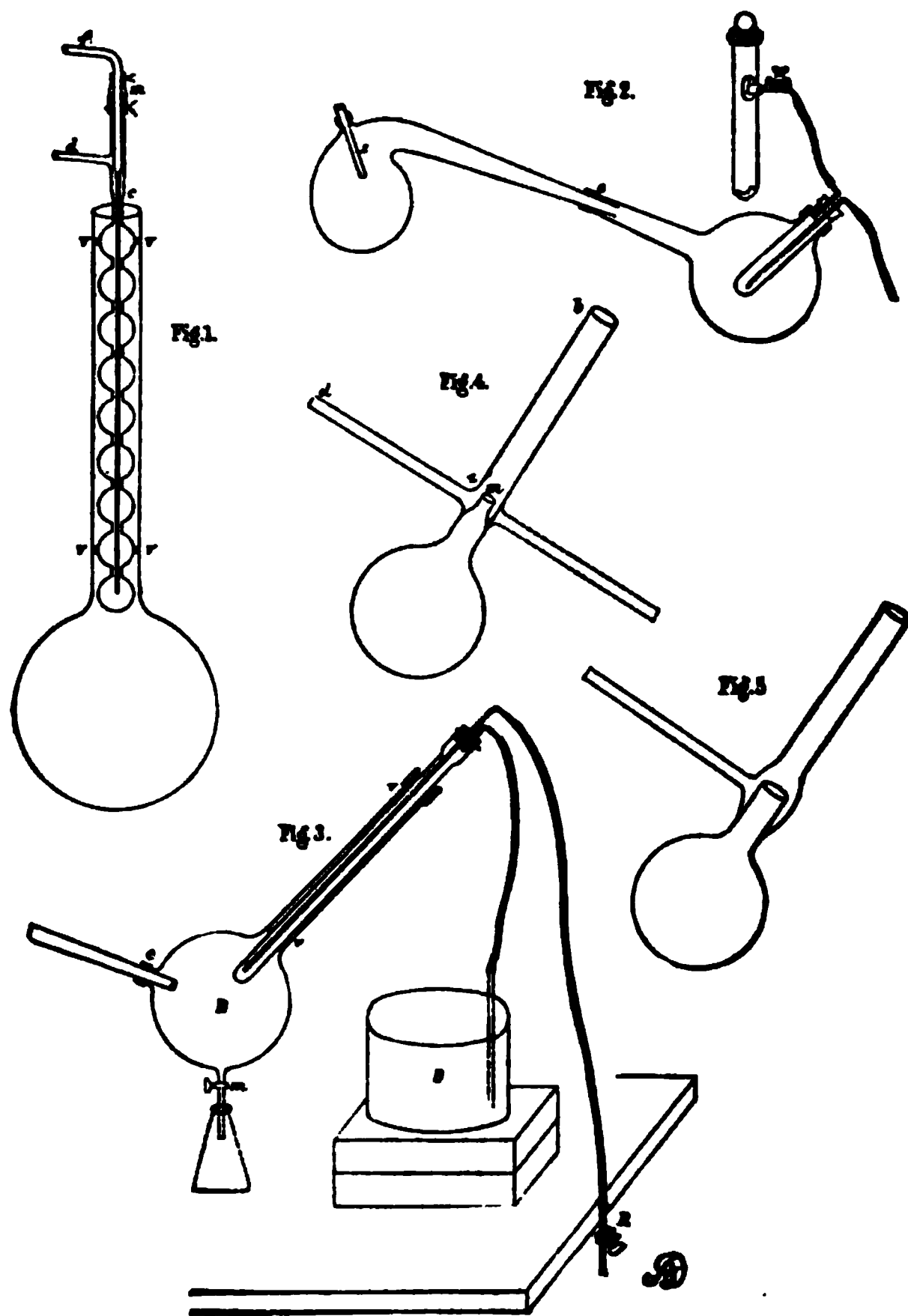
FIG. 2.

Front View of Apparatus.

[In a note to the editor Mr. Jones states that he learns, upon the authority of Prof. Stillman, that the "blast aspirator" mentioned above is the invention of Mr. E. A. Uehling and not of Mr. Yuengling, as stated in his paper. *E. H.*]

Apparatus for Chemical Laboratories.—Joh. Walter, Jour. prak. Chem., 34, 427. Fig. 1 is a condenser to be used in place of the ordinary inverted Liebig's condenser, the cooling water passing in through the tube *f* and out through *d*, or the

current can be passed in the opposite direction, entering at *d* and passing out at *f*. Fig's 2 and 3 show the same principle applied to the receiver of a retort, Fig. 2 for high boiling and Fig. 3 for very volatile liquids, *D* being filled with ice water; this apparatus can also be used for fractional distilla-



tions, the fractions being drawn off through *m*. *z* in Fig. 2 is a glass tube closed at the lower end and ground into the neck of the retort. It is used for receiving the thermometer in distilling liquids which attack cork or rubber, a little mercury being first poured into the tube.

Fig. 4 shows a distilling flask arranged so that the distillate

can either be run back into the flask or collected separately. A condensing tube is inserted in the neck of the flask and the condensed liquid collects in the neck and runs back into the flask, when, however, the tube *d* is turned into the position shown by the dotted line the distillate passes off and is collected in a receiver. Fig. 5 shows a slightly different form of the same apparatus.

A New Apparatus for Determining the Calorific Power of Coal.—W. Thomson, Jour. Soc. Chem. Ind., 5, 581. The coal is burned in a platinum crucible in a stream of oxygen and the products of combustion passed through a known weight of water, the temperature of which is noted at the beginning and end of the experiment. The apparatus consists of a narrow, tall beaker filled with water. In this the combustion chamber is placed and during the burning the gases escape from the bottom of the combustion chamber and pass up through the water, being broken up in their ascent by disks of wire gauze which fill the space between the walls of the beaker and the combustion chamber. The combustion chamber consists of an inverted test-tube 6 by 1½ inches, drawn out, so that oxygen can be introduced at the top. A bottom is provided which is held in place by means of springs pressing against the outside of the tube. On this bottom is placed the crucible supported on a cylinder of pipe clay. The coal is ignited by means of a fuse of lamp wick soaked in potassium nitrate. The author also describes a special form of gasholder for securing a steady current of oxygen. For this and for further details the reader is referred to the original paper.

Ferric Chloride as an Exciting Agent for Voltaic Batteries.—H. N. Warren, Chem. News, 55, 49. A strong solution of ferric chloride mixed with bromine may be used instead of the bichromate solution in the bichromate battery. This gives a very powerful current. "Two half-pint cells decomposing water most energetically, and three smaller cells heated to intense whiteness two inches of fine platinum wire; whilst four large cells, charged with the same solution, gave

an intense arc between two graphite points, and very perceptibly volatilized platinum.”

New Method for Vapor Density Determinations.—L. F. Nilson and Otto Pettersson, *Ann. de Chim. et Phys.* [6], 9, 554. The apparatus used is a modification of that of Victor Meyer, by which the temperature of the experiment is also determined at nearly the same time as the vapor density. For this purpose the graduated tube of the Meyer apparatus is made to serve as an air thermometer, and the detrimental effect of the stem of the platinum reservoir and the connecting tubes neutralized by means of a system of compensating tubes of exactly the same volume and exposed to the same temperature. The two systems are connected by a differential manometer of capillary tubing by which the slightest difference of pressure is detected. The entire apparatus being filled with pure, dry carbon dioxide at 0° C., the platinum reservoir is then heated in a Perrot furnace until the temperature is constant, and the exact temperature then calculated by the expansion of the gas, measured by the graduated tube. The volatile substance is then immediately dropped into the heated reservoir, and the density of the vapor produced calculated by the difference between the two readings of the graduated tube, before and after the volatilization of the substance. The two determinations can thus be made within one or two minutes of each other. The extreme delicacy of the differential manometer enables both to be made with extraordinary accuracy. A very high temperature, as high as 1502° C., can be attained by the use of this apparatus, the authors having determined the vapor density of glucinum chloride at the above temperature. As a mean of four determinations of the vapor density of this chloride, made at temperatures ranging from 1080° to 1502° C., they obtained the value 2.77, a result which agrees exactly with the theoretical density, calculated from the formula, $\text{GlCl}_2=80$. For details of the apparatus and operation the reader must consult the original paper.

I. A. P.

Solubility of Gypsum in Ammonium Salts.—S. Cohn, *Jour. für prak. Chem.*, **35**, 43. The necessary space for a satisfactory abstract of this article is not at our disposal and we must refer to the original paper. The author has determined the solubility of gypsum in solutions of ammonium chloride, nitrate, sulphate and carbonate of varying strengths.

INORGANIC ANALYSIS.

Separation of Sodium and Potassium from Lithium.—F. A. Gooch, *Chem. News*, **55**, 18, 29, 40, 56 and 78. "To the concentrated solution of the chlorides, amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a temperature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is small it will now be found in solution, and the chlorides of sodium and potassium will be in the residue, excepting the traces for which correction will be made subsequently. If, however, the weight of lithium present exceeds ten or twenty milligrams, it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol previously dehydrated by boiling is to be used, and the filtrates are to be measured apart from

the washings. In filtering it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of .00041 gms. for every 10 c. c. of amyl alcohol in the filtrate exclusive of washings if the insoluble salt is entirely sodium chloride, .00051 gms. for every 10 c. c. if potassium chloride constitutes the residue, and if both sodium and potassium chlorides are present .00092 gms.; but, the entire correction may in any case be kept within narrow limits, if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the latter driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of .00050 gms. is to be made if sodium chloride constitutes the precipitate, .00059 gms. if potassium chloride alone is present in the residue and .00109 gms. if both of these chlorides are present, for every 10 c. c. of filtrate exclusive of washings."

Calcium and magnesium chlorides may be separated from the chlorides of potassium and sodium in the same way provided the treatment with amyl alcohol is repeated. The test analyses (for which reference is made to the original paper) show that the method is a good one.

Separation and Estimation of Boric Acid.—F. A. Gooch, Proc. Amer. Acad. Arts and Sci. 1886–87; Chem. News, 55, 7. The borate is treated with nitric or acetic acid and methyl alcohol and the boric acid distilled off with the alcohol, converted into calcium borate by digestion and final ignition with lime and the amount of boric acid determined from the increase in weight of the lime. "The apparatus . . . consists essentially of a retort, condenser and bath for heating. For the last I have used a paraffine bath, as being on the whole the most convenient. The condenser is set vertically, to facilitate changing the level of the retort within the bath, and to se-

cure at the same time continual and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle'' and bending the other end into the shape of a goose-neck. ''To the former end is fitted by a rubber stopper or section of tubing, a glass funnel-tube provided with a stop-cock ; the end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus, but it is convenient to attach, to receive the distillate, a small Erlenmeyer flask which moves with the condenser and is joined to it . . by means of a thistle tube and a rubber stopper, grooved to permit the free passage of air. In carrying out a distillation, the liquid to be distilled is introduced into the retort either by the funnel tube or previous to its insertion ; the glass cock is closed, the water started through the condenser, and the retort lowered into the hot paraffin, care being taken to begin the operation with the retort not more than half full and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked, it may sometimes happen that the sudden and violent explosion of the air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty, and requires little care. The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a 200 c. c. pipette makes a retort of convenient dimensions, neither too large for the distillation of small charges, nor too small to permit the treatment of 100 c. c. of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it ; 0.7 cm. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid which is to be distilled boils, —something between 130° and 140° does very well for water. and is not too high for methyl alcohol,—and under such circumstances, and when the retort is entirely submerged, it

often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet without actual boiling.

With such an apparatus the following experiments were made. The boric acid was weighed, as before, in solution, and to bring the condition of the experiment to that of an actual analysis, one gram of pure sodium hydrate was added in solution, nitric acid or acetic acid to acidity and a little more, the whole was introduced into the retort and distilled to dryness.

In those experiments in which nitric acid was employed the methyl alcohol was introduced upon the residue thus dried in six successive portions of 10 c. c. each, and distilled to dryness; but in order to break up the residue of sodium nitrate, which by its insolubility might effect to some extent the protection of the boric acid from the action of alcohol, 2 c. c. of water were introduced and evaporated between the second and third, and again between the fourth and fifth distillations.

When acetic acid was made use of to free the boric acid, the six distillations with methyl alcohol were made as before; but, sodium acetate being soluble in methyl alcohol, the intermediate treatments with water were unnecessary. With the fourth portion of methyl alcohol a few drops of acetic acid were added to preserve the acidity of the residue, which, as has been pointed out, tends to become alkaline under the treatment.

The residues of both processes of treatment were found to be free from boric acid by the exceedingly delicate test with turmeric, care being taken in the series of experiments in which nitric acid was used to oxidize nitrites by means of bromine (expelling the latter before making the test) and in the acetic acid series to acidify with hydrochloric acid sufficiently to counteract the tendency of the acetate by itself to brown the turmeric on evaporation. The lime to retain the boric acid in the distillate was ignited in the crucible in which the evaporation of the distillate was to be made subsequently, and then transferred to the receiving flask attached to the condenser, so that the boric acid might be fixed during the distillation. To prevent

the caking of the lime by the action of the alcohol, it was slaked with a little water before the distillation was begun.

In experiments 13 to 16 nitric acid was employed and in 17 to 20 acetic acid was used, with the precaution noted, to liberate the boric acid."

In presence of chlorides nitric acid cannot be used to liberate the boric acid and acetic acid must be used. In 21 to 23 .5 gms. sodium chloride were added before each distillation and the distillation carried out with acetic acid as above described. Sodium acetate in moderate amount does not seriously interfere, but any large amount of potassium acetate is disadvantageous. Where chlorides are present an alternative method is to precipitate the chlorides with silver nitrate and distill the filtrate with nitric acid. It is necessary that the lime should remain in contact with the alcoholic distillate for from five to fifteen minutes with frequent stirrings in order that the boric acid may have time to combine with it.

<i>No.</i>	<i>B₂O₃ taken Gms.</i>	<i>CaO taken Gms.</i>	<i>B₂O₃+CaO found Gms.</i>	<i>B₂O₃ found Gms.</i>	<i>Error Gms.</i>
13	.1738	.9647	1.1392	.1745	.0007+
14	.1806	.9639	1.1456	.1817	.0011+
15	.1779	.9665	1.1450	.1785	.0006+
16	.1824	.9739	1.1587	.1848	.0024+
17	.1806	1.4559	1.6371	.1812	.0006+
18	.1812	.9720	1.1543	.1823	.0011+
19	.1788	.9986	1.1781	.1795	.0007+
20	.1813	.9527	1.1358	.1831	.0018+
21	.1834	.9842	1.1675	.1833	.0001—
22	.1831	.9755	1.1593	.1838	.0007+
23	.1761	.9740	1.1523	.1783	.0022+

Estimation of Boric Acid.—Th. Rosenblatt, Zeit. anal. Chem. 26, 18. The method is identical with that of Gooch described above, except that magnesia is used to combine with the boric acid in the distillate, and that the apparatus used in the distillation is different. Using crystallized boric acid

99.89 to 99.99 per cent. of the acid present was obtained ; from crystallized borax 99.77 to 99.92 per cent. ; from barium borate 99.74 to 99.82 per cent. ; from calcium borate 99.77 to 99.83 per cent. ; from a fused mixture of feldspar and boric acid 99.80 to 99.92 per cent. A sample of tourmaline fused with sodium carbonate and treated by this method gave 8.60 to 8.65 per cent. B_2O_3 . The author remarks that the methyl alcohol used should be free from aldehyde and other substances which cause blackening when mixed with sulphuric acid.

Properties and Analysis of Chloride of Sulphur.—Chas. A. Fawsitt, Jour. Soc. Chem. Ind., 5, 641. The chloride of sulphur of commerce consists of a mixture of S_2Cl_2 and SCl_2 , the former predominating in the yellow and the latter in the darker colored varieties. The composition of different samples is shown below :

	No. 1	No. 3	No. 5	Calculated for	
				S_2Cl_2	SCl_2
Sulphur	47.33	48.30	39.67	47.41	31.07
Chlorine	52.09	51.27	60.03	52.59	68.93

Nos. 1 and 3 are yellow, No. 5 is a red sample.

The specific gravity of No. 1 was 1.682, of No. 3, 1.6846 and of No. 5, 1.657, water at $15.5^\circ C=1$.

For vulcanizing rubber the yellow varieties are much more suitable than the red. When chloride of sulphur is mixed with water, sulphur dioxide, sulphuric acid, free sulphur and hydrochloric acid are formed. A small amount of H_2S is formed at the ordinary temperature and probably tetrathionic or pentathionic acid.

ANALYSIS.

“In the analysis of chloride of sulphur a precaution to be attended to at the outset is not to expose the samples too freely to the atmosphere, as they soon change in their composition, and to avoid this in weighing the best plan is to partly fill a small, thin glass tube with drawn out end by warming gently and then allowing a little to be drawn in as the air cools. This is boiled, and when the bulb is deemed full of vapor the

end is immersed in the liquid which then rises and almost completely fills it; the bulb is now sealed and weighed. In the case of the dark variety care should be taken to boil out completely before filling for the last time, as if any were left in the bulb it would have a different composition from the sample.

To Determine the Sulphur.—Measure into a small flask about 25 c. c. of strongest HNO_3 ; the bulb containing the chloride is now dropped in and broken, and to moderate the reaction the flask is kept immersed in cold water. If any undecomposed sulphur now remains, the flask is gently warmed in a slanting position and a crystal of chlorate of potash added occasionally until it is all oxidized; the contents of the flask are transferred to a basin, the excess of HNO_3 removed by evaporation in a water bath with HCl ; taken up with water and the H_2SO_4 precipitated and weighed as BaSO_4 .

For Chlorine.—A bulb containing about 2 gms. is broken under water or weak NaOH solution in a 250 c. c. stoppered flask, the contents well shaken, and when decomposition is complete allowed to settle. A weighed or measured portion is transferred to a flask, and the liquid, if acid, made alkaline with Na_2CO_3 ; it is now boiled, HNO_3 added, and if any sulphur has separated out, filtered, the HCl in the filtrate is precipitated and weighed as AgCl .

For Estimating "Chromate" in "Bichromate."—N. McCulloch, Chem. News, 55, 2. The method is founded upon the fact that hydrogen dioxide only converts free chromic acid, not chromate nor bichromate, into perchromic acid. The method is described as follows: "5 or 10 grams of the sample are placed in a test-tube, 4 centimeters in diameter and $\frac{1}{4}$ meter or so in length and dissolved in a small quantity of water. A few c. c. of hydrogen peroxide (10 vols) are added, and the whole covered with a layer of sulphuric ether 3 centimeters in depth. The mouth of the test-tube is now stopped with a paraffined cork, pierced in the centre with a short glass tube for admitting the standard sulphuric acid, which is run in from a burette in small quantities at a time, with agi-

tation after each addition, until the layer of ether is tinged faintly blue, as best seen against a white background. By calculating the equivalent of acid consumed to two equivalents of chromate of soda or potash, as the case may be, we obtain the chromate in the portion of the sample taken.

Judging from the very dark color that peroxide of hydrogen imparts to salts of bichromic acid a perchromate seems to be formed and is insoluble in ether. The existence of that color is a convenient indication in this process of the peroxide of hydrogen which has escaped decomposition during titration, and unless that quantity is such as to render the color of the liquid practically opaque about the completion of the operation, a further addition of that reagent will be necessary."

The following results were obtained:

Value of Test Acid calc. from Experiments 1 and 2, 1 c. c. = .0113 gms. Na_2CO_3 = .04148 gms. K_2CrO_4 .

Calculated from 4 and 5, 1 c. c. = .011236 gms. Na_2CO_3 = .4124 gms. K_2CrO_4 .

No. of Expt.	Indicator.	Material & amt. used.	c. c. Test Acid Added.	Quantity found calculated from 1 and 2.	Quantity found calculated from 4 and 5.
1	Litmus	1.6197 Na_2CO_3	143.34		
2	"	1.6197 "	143.34		
3	H_2O_2 and Ether.	1.6197 Na_2CO_3 + .32 $\text{K}_2\text{Cr}_2\text{O}_7$	143.99	1.6268	
4	"	1.6197 Na_2CO_3 + 1.62 $\text{K}_2\text{Cr}_2\text{O}_7$	144.15	1.6288	
5	"	.6479 Na_2CO_3 + 3.2 $\text{K}_2\text{Cr}_2\text{O}_7$	57.66	.6511	
6	"	3.2394 K_2CrO_4	78.20	3.2433	3.2245
7	"	"	78.39	3.2518	3.2330
8	"	"	78.33	3.2485	3.2297
9	"	.6479 K_2CrO_4 + 3.24 $\text{K}_2\text{Cr}_2\text{O}_7$	15.73	.6524	.6491
10	"	.01296 K_2CrO_4 + 3.24 $\text{K}_2\text{Cr}_2\text{O}_7$.32	.1295	.1295
11	"	.00648 K_2CrO_4 + 3.24 $\text{K}_2\text{Cr}_2\text{O}_7$.19	.0077	.0077

The Solubility of Nitrogen Dioxide in Sulphuric Acid.—A discussion upon this subject between Lunge and Bayley has been going on for some time in the columns of the Chemical News. (See 53, 6, 266, 289; 54, 6, 27, 52.) Bayley asserts that the ordinary *pur.* acid used in the nitrometer contains

iron which dissolves the nitric oxide, at the same time some of the iron is reduced to the ferrous condition. Lunge fails to find any reduction of iron to the ferrous state, asserts that ferric salts do not dissolve nitric oxide, and says that even if nitric oxide is dissolved by ferric salts no proof has been given that enough iron is contained in ordinary vitriol to affect the results.

F. Nettlewood has now taken up the matter with a view to determine whether any correction is necessary in the use of the nitrometer, and if so how much (Chem. News, 55, 28). He finds that when .3 gms. gun-cotton is dissolved in 7 c. c. H_2SO_4 , 59.7 c. c. nitric oxide is obtained. On introducing 16.7 c. c. additional H_2SO_4 , 58.4 c. c. nitric oxide remain, or each c. c. H_2SO_4 dissolves .08 c. c. nitric oxide.

In two other experiments with gun-cotton, the figures .057 and .057 were obtained.

In two experiments with potassium nitrate treated in a similar manner it was found that 1 c. c. H_2SO_4 absorbed .2 and .09 c. c. of nitric oxide.

On shaking pure nitric oxide with pure sulphuric acid no absorption took place.

It seems, therefore, that a correction is needed, but that the correction to be applied differs with the nature of the substance analyzed.

Indirect Estimation of the Haloids.—J. E. Whitfield, Amer. Chem. Jour., 8, 421. The author finds that the silver haloid salts may be dissolved in potassium cyanide and the silver precipitated by electrolysis. 4 Meidinger cells of large size give a current of the proper strength. If all the haloids are present iodine is first removed and determined separately. The bromine and chlorine are then precipitated by adding silver nitrate. The precipitate is filtered through a Gooch crucible with gentle pressure, dried directly over the flame at a low temperature and weighed; the precipitate is then dissolved by introducing the crucible into a strong solution of potassium cyanide. In some cases metallic silver remains in the asbestos; when this happens it is dissolved in a little nitric

acid and added to the main solution. A little ammonia is added and the silver precipitated by electrolysis and weighed. Not more than 2 gms. of the silver salt should be employed. The solution is removed from the dish immediately on the stopping of the current, or better, siphoned off while the battery connections are still unbroken. The results given below were obtained from silver chloride. In (1)–(3) the silver chloride was dissolved in potassium cyanide, and a little caustic soda added; in the others ammonia was used instead. In (4) and (5) the chloride was dissolved in potassium cyanide, potassium bromide added, the solution precipitated with sulphuric acid, the silver bromide redissolved in potassium cyanide, ammonia added and the solution subjected to electrolysis.

	<i>AgCl taken.</i>	<i>Silver found.</i>	<i>Silver Calculated.</i>	<i>Error.</i>
(1)	0.1565 gms.	0.1177 gms.	0.1178 gms.	.0001 gms.—
(2)	1.3004 “	0.9785 “	0.9787 “	.0002 “ —
(3)	2.2657 “	1.7047 “	1.7051 “	.0004 “ —
(4)	0.7472 “	0.5618 “	0.5624 “	.0006 “ —
(5)	0.2854 “	0.2133 “	0.2147 “	.0014 “ —

The author has also examined the method of Maxwell–Lyte which consists in converting the mixture of silver chloride, bromide and iodide into a mixture of bromide and iodide by dissolving in potassium cyanide adding potassium bromide equal in weight to the silver salts taken and precipitating with sulphuric acid. The mixture of bromide and iodide is weighed, again dissolved in potassium cyanide, potassium iodide added, converting the silver into iodide, which is then precipitated with sulphuric acid and again weighed. The results show that the conversion of chloride into bromide is imperfect, but that conversion of either chloride or bromide into iodide gives satisfactory results.

The following are the results obtained:

ESTIMATION OF THE HALOIDS.

AgCl Tak- en.	AgBr Found.	AgBr Calcu- lated.	Error.	Equivalents KBr Taken.	Silver Found.	Silver Calcu- lated.	Error.
(6) 0.3260 gms.	0.4227	0.4270	.0043—	2	0.2443	0.2453	.0010—
(7) 0.3093 "	0.4023	0.4052	.0029—	2			
(8) 1.3801 "	1.8041	1.8080	.0039—	2	1.0385	1.0386	.0001—
(9) 0.2091 "	0.2723	0.2739	.0016—	10			
(10) 0.6846 "	0.8909	0.8968	.0059—	10	0.5137	0.5152	.0015—
(11) 1.1625 "	1.5202	1.5230	.0028—	20			
(12) 1.1734 "	1.5310	1.5372	.0062—	20	0.8829	0.8831	.0002—
(13) 0.3501 "	0.4553	0.4586	.0033—	29	0.2634	0.2634	.0000
(14) 0.4178 "	0.5468	0.5473	.0005—	29			

AgCl Tak- en.	AgI Found.	AgI Calcu- lated.	Error.	Equivalents KI Taken.	Silver Found.	Silver Calcu- lated.	Error.
(15) .6996 gms.	1.1451	1.1456	.0005—	2	.5255	.5265	.0010—
(16) .7587 "	1.2429	1.2424	.0005+	2	.5691	.5710	.0019—
(17) .6710 "	1.0992	1.0988	.0004+	10	.5042	.5050	.0008—
(18) .2515 "	0.4118	0.4118	.0000	10	.1892	.1892	.0000
(19) .6501 "	1.0646	1.0646	.0000	10	.4892	.4892	.0000

Silver Tak- en.	AgI Found.	AgI Calcu- lated.	Error.	Equiva- lents KI.	Silver Found.	Error.
(20) .5418 gms.	1.1790	1.1789	.0001+	2	.5417	.0001—
(21) .3750 "	0.8154	0.8159	.0005—	2	.3746	.0004—
(22) .4078 "	0.8859	0.8873	.0012—	10	.4077	.0001—

Estimation of Sulphur in Soluble Slags.—E. D. Campbell, Chem. News, **55**, 74. “.5 gm. of the finely pulverized slag is introduced into a cold solution made by taking 25 c. c. hydrochloric acid sp. gr. 1.19, adding 50 c. c. water and 5 c. c. bromine. A little free bromine is left on the bottom of the beaker. The solution is allowed to stand cold for a few minutes and then gradually raised to a boil, and the boiling continued until the bromine is entirely driven off. The solution is then filtered, a solution of barium chloride added, the whole nearly neutralized with ammonia, and boiled until the barium sulphate has settled to the bottom. The barium sulphate is then filtered off, washed, ignited and weighed as usual.”

Volumetric Estimation of Nitrous Acid.—A. G. Green and F. Evershed, Jour. Soc. Chem. Ind. **5**, 633. A modification of the process of Green and Rideal, (Chem. News, **49**, 173). The normal aniline solution contains 93 gms. pure aniline and about 450 c. c. hydrochloric acid in 1 liter. Of this solution 25 c. c. is placed in a small stoppered bottle with a little ice. The solution of the nitrite (about normal) is then run in from a burette with continual agitation. From time to time a drop is taken from the bottle and mixed on a white slab or dish with a drop of a solution of potassium iodide and starch. The *immediate* production of a blue color indicates the presence of nitrous acid in excess. If, after some minutes, another test shows that the nitrous acid has been taken up, another drop is added from the burette, and so on until there is an excess after the solution has stood for an hour. By the quantity of nitrite used, omitting the last drop, its value in HNO_2 or NaNO_2 is indicated. Results obtained by this method were compared with those obtained by a slight modification of the process of Kinicutt and Nef, (Amer. Chem. Jour., **5**, 388) as follows:

SODIUM NITRITE IN STICKS, SOLD AS PURE, PERCENTAGE OF NaNO_2 .

Aniline Process.		Permanganate Process.	
1	97.27 per cent.	1	97.40 per cent.
2	97.27 “	2	97.65 “
3	97.01 “	3	97.60 “
4	97.09 “		

COMMERCIAL NaNO_2 ,		ANILINE PROCESS ONLY.	
1	95.06 per cent.	4	94.86 per cent.
2	94.88 "	5	95.13 "
3	95.05 "	6	95.04 "

In the discussion which followed the reading of the paper Mr. Evershead stated that the advantage of the method over the permanganate process lay in the fact that permanganate would oxidize other substances besides nitrous acid while the aniline was affected by this substance alone.

Testing for Ammonia, Nitrous or Nitric Acid and Thiosulphates, in a mixture of alkaline salts.—L. L. de Koninck, Zeit. anal. Chem. 26, 26. The solution is put into a flask connected by means of a cork and bent tube with a U tube containing a little Nessler's solution. A little sodium hydroxide is added to the contents of the flask and the solution boiled. Any ammonia present alters the color of the Nessler's solution. The boiling is continued until the ammonia is all driven off. A few pieces of aluminum foil are then added and, after standing for some time, distilled again into some fresh Nessler's solution. In the solution left in the flask the thiosulphate will have been converted into sulphide, $\text{M}_2\text{S}_2\text{O}_3 + 2\text{NaOH} + \text{H}_2 = \text{M}_2\text{SO}_3 + \text{Na}_2\text{S} + 2\text{H}_2\text{O}$, which can be detected by means of sodium nitroprusside.

On the Precipitation and Washing of Alumina.—S. L. Penfield and D. N. Harper, Am. Jour. Sci., III, 32, 112. When alumina is precipitated in a solution containing ammonium chloride or nitrate, it is apt to become sticky on washing with water and to pass through the filter. This can be obviated by washing with a solution of ammonium nitrate made by neutralizing 2 c. c. concentrated nitric acid with ammonia and diluting to 100 c. c.

Alumina precipitated from solutions containing ammonia salts (4 to 8 c. c. concentrated hydrochloric or nitric acid) is easier to filter and wash than when thrown down from solutions containing less saline matter. When a second precipitation is necessary in order to free the alumina from fixed salts it is best to dissolve in nitric instead of hydrochloric acid.

Volumetric Estimation of Chromium.—W. J. Sell, Chem. News, 54, 299. When chromium hydroxide is treated in alkaline solution with hydrogen dioxide it is converted into chromic acid as follows:



The author has founded a volumetric method for the estimation of chromium upon this reaction. A solution containing a known weight of chrome alum was taken, a certain volume treated with caustic potash in excess, to dissolve the precipitate at first formed, hydrogen dioxide added and the solution boiled for fifteen minutes; the chromic acid was then determined by the idiometric method (Zulkowsky's modification). The following results were obtained:

(Theoretical percentage of chromium in chrome alum = 10.49.)

Gms. Cr. Alum Taken.	c. c. Thiosulphate used.	1 c. c. Thiosulphate = Gms. Cr.	Cr. Obtained.	Per Cent. Cr.
.60579	37.2	.001709	.06357	10.49
.60579	37.4	"	.06391	10.56
.60579	37.6	"	.06425	10.60
.5677	39.5	.00151	.05964	10.50
.75542	53.	"	.08003	10.59
*.75542	53.1	"	.08018	10.61
1.0159	66.6	.001613	.10742	10.57
†.7889	56.9	.00151	.0859	10.89

*To this lot, after addition of the oxidizing mixture and boiling ten minutes, a small quantity of platinum black was added and the boiling continued for a further period of ten minutes.

†This lot was only boiled ten minutes after addition of the oxidizing mixture.

Some additional experiments were made with .5 potassium dichromate; in the first place determining the chromium in 50 c. c. of the solution, and then repeating the determination on 50 c. c. in which the chromium had first been reduced to hydroxide and then re-oxidized as above. The following are the results obtained:

	Thiosulphate.
(1) 50 c. c. dichromate required . .	68.5 c. c.
(2) " " " " . .	68.6 "
(3) " after reduction and oxidation.	68.6 "
(4) " " " " " "	68.2 "

Two other experiments, in which potash was replaced by sodium carbonate, gave equally satisfactory results.

INFLUENCE OF OTHER METALS.

Alumina.—.75542 gms. chrome alum, and about an equal weight of aluminum sulphate, required thiosulphate equal to 10.37 per cent. chromium.

.75542 gms. chrome alum, and as much aluminum sulphate, required thiosulphate equal to 10.46 per cent. chromium.

Zinc.—50 c. c. .% potassium dichromate, and about 1 gm. zinc sulphate, when reduced and oxidized required 68.6 c. c. thiosulphate.

Iron.—As ferric salts liberate iodine from potassium iodide a modification of the method was necessary. After oxidation the ferric hydroxide was filtered off and the chromium determined in the filtrate, as before.

.60579 gms. chrome alum, mixed with ferric chloride, required thiosulphate equal to 10.29 per cent. chromium. 50 c. c. .% dichromate, reduced and oxidized in presence of ferric chloride, required 68.5 c. c. thiosulphate.

50 c. c. as above required 66.8 c. c. thiosulphate.

The above method of estimating chromium may also be used in qualitative analysis for the detection and separation of chromium from metals of the third group (those precipitated by ammonium hydroxide.)

Separations by Means of the Alkaline Thiocarbonates.—Th. Rosenbladt. Zeit. anal. Chem., **26**, 15. The sulphides of those metals which form ammonio compounds (cobalt, nickel, mercury and palladium) dissolve in the alkaline thiocarbonates. From such a solution containing mercury and palladium the former is precipitated by carbon dioxide, while palladium remains in solution.

Preparation of Potassium Thiocarbonate.—1 part of sulphur is dissolved in 2 parts CS₂ and 15 parts KOH solution sp. gr. 1.13 added and the mixture digested for several days with frequent shaking until the liquid takes an orange color. The solution is then poured off from the CS₂ which is again treated

in the same way with 8 parts KOH solution. If the CS_2 becomes colorless more sulphur must be added to it. 10 c. c. of such a solution will dissolve about .2000 gms. sulphide of mercury.

Separation of Mercury from Palladium.—50 c. c. of a solution (A) containing mercuric chloride equal to .116 gms. HgS were mixed with 25 c. c. of a solution (B) of palladium chloride containing .10 gms. palladium and 30 c. c. of the thiocarbonate solution added and the mixture warmed. Washed carbon dioxide was then passed through the solution and the precipitated HgS washed with water, dried, the sulphur extracted with CS_2 in Soxhlet's extraction apparatus and the remaining HgS weighed: obtained .1159 gms. HgS . From the filtrate .0999 gms. palladium was obtained.

Separation of Mercury from Lead.—50 c. c. mercuric chloride solution (A) and 50 c. c. of lead acetate, containing about .5 gm. Pb., was precipitated with H_2S , boiled with 30 c. c. thiocarbonate solution for half an hour, filtered and washed, the filtrate acidified with HCl and the HgS filtered off, washed, dried, the sulphur extracted with CS_2 and the HgS weighed: obtained .116 gms. HgS . The filter ash was free from lead.

Separation of Mercury from Copper.—50 c. c. mercuric chloride solution (A) and 50 c. c. cupric chloride, containing .5 gms. Cu, treated as above, but precipitated with CO_2 instead of HCl , gave .1162 gms. HgS . In the filter ash copper could be detected with the blowpipe.

Separation of Mercury from Silver.—50 c. c. solution (A) and 50 c. c. silver solution (about .5 gms. Ag) treated as above gave .1159 gms. HgS .

Separation of Mercury from Bismuth.—50 c. c. solution (A) and 50 c. c. bismuth solution (about .5 gms. Bi) treated as above gave .1158 gms. HgS .

Cadmium cannot be separated from mercury by this method.

Separation of Palladium and Mercury from Lead, Copper and Bismuth.—50 c. c. solution (A) 25 c. c. solution (B), and about .1 gm. each of salts of lead, copper and bismuth treated

with 50 c. c. thiocarbonate solution as above gave .1157 gms. HgS and .0997 gms. palladium.

Colored Reactions of the Rare Mineral Acids.—Lucien Levy. Comptes Rendus, 103, 1074, 1195. The reagents used are either phenols or bodies allied to the phenols in some of their properties. The mode of operation is as follows: a trace of the reagent (not more than $\frac{1}{4}$ milligram) is moistened with eight drops of sulphuric acid, placed on a watch-glass, and a few grains of the powdered acid, or one of its salts, added. If stannic acid is to be tested for, it is necessary to use a somewhat larger quantity of the substance, and to add a few drops of water. The results obtained with titanic, niobic, tantalic and stannic acids are given in the following tables:

COLORATIONS GIVEN BY

Reagents.	Titanic Acid.	Niobic Acid.
Morphine	Crimson.	None.
Codeine	None.	{ Mauve, slowly appearing.
Brucine	Light Crimson.	Brownish Yellow.
Phenol	Brick Red.	Yellow.
Alpha Naphthol	{ Greenish, then Violet.	{ Green, then Slate Gray.
Beta Naphthol	Coffee Brown.	Gamboge.
Thymol	Granite.	{ Flesh Color, then Brown.
Resorcine	{ Flesh Color, then Chocolate.	Yellowish.
Hydroquinone	Crimson.	{ Dirty Gray, then Mauve Violet.
Pyrocatechine	Chocolate.	Pearl Gray.
Pyrogallol	{ Crimson, then Brown.	{ Greenish Gray.
Salicylic Acid	{ Flesh Color, then Brick Red.	{ Rose, then Flesh Color.
Meta-oxybenzoic Acid	{ Chrome Yellow	Bright Yellow.
Para-oxybenzoic Acid	{ Chrome Yellow	None.
Gallic Acid	Brick Red.	None.

Reagents.	COLORATIONS GIVEN BY	
	Tantallic Acid.	Stannic Acid and Water.
Morphine	Yellow, then Brown.	None.
Codeine.	Sea Green.	None.
Brucine	Tea Rose.	None.
Phenol	{ Rose, then Green, then Rose, on ad- dition of water. }	None.
Alpha Naphthol. .	Scheele's Green	Amethyst Violet.
Beta Naphthol. . .	Greenish.	Apple Green.
Thymol	{ Yellow, then Green, then Olive. }	Light Rose.
Resorcine	{ Dirty Gray, then Am- ethyst Violet, then Rose. }	Orange.
Hydroquinone . .	{ Greenish, then Yel- low. }	Light Yellow.
Pyrocatechine . . .	Greenish.	Light Yellow.
Pyrogallol	Greenish.	Tea Rose.
Salicylic Acid. . .	{ None, black the next day. }	None.
Meta-oxybenzoic Acid	{ Very Bright Yel- low. }	None.
Para-oxybenzoic Acid	{ None, greenish the next day. }	None.
Gallic Acid	None.	None.

With the exception of that produced by stannic acid, all these colorations disappear on the addition of a few drops of water. The coloration obtained with brucine, however, remains after the addition of water. It is necessary that the bodies operated upon be entirely free from any nitric or nitrous acid compounds as the nitrous vapors produced by the sulphuric acid give derivatives of a very intense coloration.

The preceding tables show that nearly all the reagents used possess one or more of the properties of the phenols. Brucine, however, has not heretofore been considered as a phenol. On the other hand, the acids, alcohols, aldehydes, acetones, quinones and alkaloids, which are not allied to the phenols, do not give any coloration. This is, at least, the result of a large

number of experiments made with many different compounds.

Certain derivatives of the phenols also give the colorations with titanlic acid; thus phenylsulphuric acid gives an orange coloration, and triphenyl phosphate tea rose. Some allied hydrocarbons also give colorations. Sulpho-conjugated derivatives are first formed. Thus, benzine gives slowly a reddish yellow coloration, toluene a brownish yellow, and naphthalene a bright violet, turning to gray.

For the detection of the above four acids in presence of each other, the author proposes the following method: the mixture is first thoroughly calcined to destroy any trace of nitric acid which may be present; a portion of the mixture is then treated as above with morphine; a crimson coloration shows the presence of titanlic acid; a second portion is treated with codeine; a mauve coloration indicates niobic acid; a third part is treated with resorcine; an amethyst violet coloration, or green, if much of the other acids be present, shows the presence of tantalic acid; to a fourth part of the mixture alpha naphthol and some water is added; an amethyst violet coloration indicates stannic acid.

Conversely, we can distinguish certain phenols in presence of each other, by means of these mineral acids; thus in a mixture of morphine and codeine, titanlic acid indicates even a trace of morphine, while the codeine, if in sufficient quantity is detected by the addition of niobic acid.

Silica, alumina, zirconia, yellow oxide of uranium and phosphoric, phosphorous, tungstic and boric acids, do not give any coloration.

The following tables give the colorations produced by arsenic, arsenious and vanadic acids, and the oxides of antimony and bismuth :

Reagents.	COLORATIONS GIVEN BY		
	Arsenic Acid.	Vanadic Acid.	
		Before the Addition of Water.	After the Addition of Water.
Morphine	None.	None.	Rose, then Green.
Codeine	None.	LightGreen	{ Violet precipitate, soluble in excess of water.

Phenol	None.	Sepia.	Sepia.
Thymol	Sepia.	Yellowish.	Rose.
Alpha Naphthol.	Green.	Green.	Bright Green.
Beta Naphthol .	Brown.	Green.	Bright Green.
Resorcine . . .	Sepia.	Dark Green.	Violet.
Hydroquinone .	Yellowish.	Greenish Yel.	Green.
Pyrocatechine	{ Greenish gray then amethyst violet. }		Dk Green. Green.
Pyrogallol . . .	Brown.	Sepia.	Rose.
Salicylic Acid .	None.	None.	Green.
Meta-oxybenzoic Acid	{ None.	None.	Rose.
Gallic Acid . . .			
	None.	None.	Greenish.

COLORATIONS GIVEN BY

	Oxide of Bismuth.		
Reagents.	Before the addition of water.	After the addition of water.	Oxide of Antimony and Arsenious Acid.
Morphine . . .	Light Rose.	None.	None.
Codeine	Light Rose.	None.	{ Bright Lilac, with Arsenious Acid only.
Phenol	None.	Rose.	
Thymol	None.	Rose.	Flesh Color.
Alpha Naphthol .	None.	None.	Green.
Beta Naphthol . .	None.	None.	Yellow.
Resorcine . . .	None.	Orange.	Sepia.
Hydroquinone .	None.	None.	None.
Pyrocatechine .	Greenish.	Deep Green.	Flesh Color.
Salicylic Acid .	{ Green, nearly Black.	{ None.	Flesh Color.
Isomers of the preceding .			
			None.

All the colorations due to arsenic acid disappear on the addition of water, except that produced by pyrocatechine; this gives a green liquor, and finally a green precipitate. The colorations given by the oxide of antimony and arsenious acid also disappear when water is added.

Molybdic acid colors only some of the above named reagents: thus morphine becomes rose in color; resorcine, sepia; codeine and the naphthols, greenish; but all the reagents, tried with the other acids, give green precipitates on the addition of water.

It is seen by the above tables that it is possible to detect arsenic acid in presence of phosphoric and vanadic acids, by means of pyrocatechine; pyrocatechine, in presence of its isomers, with arsenic acid; vanadic acid in presence of molybdic and phosphoric acids by means of resorcine; and oxide of bismuth in presence of arsenious acid and oxide of antimony, by using pyrogallol.

The last table, compared with the one previous, shows also that arsenates can be distinguished from arsenites by pyrocatechine, and that tin can be detected, in presence of arsenic, antimony and bismuth, by means of alpha naphthol and water.

I. A. P.

The Volumetric Determination of Metallic Zinc in Powdered Zinc.—Frederic Weil, *Comptes Rendus*, 103, 1013. A standard solution of cupric chloride is first prepared. Pure copper nitrate is dried in a porcelain dish, and then completely calcined in a platinum crucible. The cupric oxide thus obtained is cooled in a desiccator, and 12.519 grams weighed out. This is dissolved with the aid of heat in a slight excess of hydrochloric acid, and the solution diluted to one liter. 10 c. c. of the liquid will then contain exactly .1 gram of metallic copper.

By means of a pipette, 50 c. c. of the solution is poured into a porcelain capsule, and ammonia added until a slight permanent precipitate remains after stirring. The liquid should still have a feeble acid reaction. .4 gram of the powdered zinc is then dropped into the bottom of the capsule and a platinum wire, coiled into the form of a spiral plane at one end, placed on top for the purpose of stirring at intervals.

The zinc precipitates its equivalent of copper. At the ordinary temperature the operation requires not more than an hour, but ten minutes only, if a platinum capsule be used.

The end of the reaction is indicated very exactly by introducing a platinum bead at the end of a platinum wire into the bottom of the capsule. If any zinc remains undissolved, the bead is immediately covered with a slight black or red coating. If, however, the operation is completed, the bead remains brilliant. The platinum spiral is then withdrawn and washed, and a little acetic acid added, drop by drop, to the solution to render it clear. The clear solution above the precipitated copper is then decanted into a glass vessel graduated to 100 c. c. or 200 c. c. The capsule and copper are well washed with distilled water, the decanted washings added to the main solution, and the whole diluted to the mark. The solution is then shaken up and allowed to stand a few minutes for the desposition of sediment. 10 c. c. of the clear liquid is placed in a white glass vessel, heated, and the copper determined, while boiling, by adding standard stannous chloride solution until complete decoloration. The strength of the tin solution is found by titrating with weak cupric chloride solution, 10 c. c. of which contains .04 gram of metallic copper.

The excess of copper used in the operation is thus determined, and by deducting this from the original amount, .5 gram, the weight of copper precipitated by the zinc is obtained. This multiplied by 1.0236

$$\begin{array}{r} \text{Zn}=32.6 \\ \hline \text{Cu}=31.75 \end{array} = 1.0236,$$

gives the weight of metallic zinc in the powdered zinc.

A specimen of powdered zinc, analyzed by the author, by this method gave 65.3 per cent. of metallic zinc. The same powder, analyzed by the exact hydrogen method of Fresenius, gave the same result, thus proving the accuracy of the new method.

I. A. P.

Separation of Aluminum and Beryllium.—S. L. Penfield and D. N. Harper, *Am. Jour. Sci.*, III, **32**, 114. The authors find the caustic soda method of separation to be the most accurate. In order to examine the method two standard solutions were made; a standard solution of beryllium chloride

containing .1107 gms. BeO in 50 c. c.; a solution of aluminum chloride containing .1002 gms. Al_2O_3 in 50 c. c. 50 c. c. of each solution were taken and evaporated to dryness in platinum, the chlorides dissolved in the smallest possible amount of water and a rather strong solution of pure sodium hydroxide added till the precipitate redissolves. No excess of soda above this must be used. The solution is then poured into 800 c. c. boiling water and the boiling continued for an hour, replacing evaporated water. The filtrate from the beryllium is acidified, concentrated and the alumina precipitated with ammonia.

The following results were obtained :

Al_2O_3 found.	BeO found.
.1041 gms.	.1093 gms.
.1057 "	.1080
—	.1096
.1045	.1099
—	.1107
.1032	.1093
.1037	.1093
.1031	.1083
—	—
Mean .1040	.1093
—	—
Contains .1002	.1107

The boiling can be conducted just as well in glass as in platinum as the soda solution is very dilute. A little of the beryllium always remains in solution and the precipitate always contains a little soda which cannot be removed by washing. The excess of Al_2O_3 in the above results is caused by BeO which remains in solution.

“When phosphoric acid is present Alumina may be separated from beryllium by boiling the solution of the mixed chlorides with barium hydroxide. The alumina goes readily into solution, while the precipitate containing the barium phosphate and beryllium is easy to filter and wash. After dissolving the precipitate and separating the barium with sulphuric acid, a beryllium phosphate can be precipitated with

ammonia. After weighing this the P_2O_5 may be determined by means of ammonium molybdate and the BeO , by difference or the precipitate may be fused with sodium carbonate and the fusion soaked out with water, which gives almost a complete separation of phosphoric acid from beryllium. If phosphoric acid is also to be determined it must be born in mind that very perceptible quantities of it will be found in the barium sulphate precipitate."

Al_2O_3 and BeO which have been ignited over a ring burner lose perceptibly in weight on ignition over a blast lamp.

Separation of Zinc from Iron, Cobalt and Nickel.—P. von Berg, Zeit. anal. Chem., 25, 512. The zinc is precipitated from its solution in formic or monochloracetic acid with sulphuretted hydrogen.

Formic Acid Separation.—The author finds that if the solution is carefully neutralized with ammonia, a little sodium formate added, then 2.5 to 5 c. c. formic acid sp. gr. 1.2, the solution diluted to about 300 c. c., heated to 50° to 60° and sulphuretted hydrogen passed through, the zinc is completely precipitated as sulphide free from iron and nickel. If cobalt is present, a little of it is apt to precipitate with the zinc; in this case the sulphide is dissolved in a little acid, neutralized, and again precipitated.

Monochloracetic Acid Separation.—The solution is neutralized with ammonia, enough ammonia added to saturate the acid present, then 7 c. c. of monochloracetic acid (378 gms. to a liter), the solution diluted to 450 c. c., heated to 50° to 60° and sulphuretted hydrogen passed through it. If the precipitate is filtered off rapidly the separation is complete, otherwise cobalt comes down as sulphide. For details and test analyses the reader must consult the original paper.

Separation of Gold and Platinum from Arsenic Antimony and Tin.—Ph. J. Dirvell, Bull. soc. chim., 46, 806. The separation is founded upon a reaction discovered by M. Silva, who finds that when the sulphides of the above metals, obtained in the ordinary course of qualitative analysis, are dis-

solved in caustic soda, chloral added, and the solution boiled; metallic gold and platinum are precipitated, leaving the arsenic antimony and tin in solution. The arsenic, antimony and tin are then precipitated from the filtrate with HCl, redissolved in HCl and separated by the method of Carnot. [This journal, I, 86.]

On the Estimation of Nickel in Mattes, Ores, Slags, Etc.— Thomas Moore, Chem. News, 54, 300. The strongly acid solution (in either nitric, hydrochloric, or sulphuric acid) is diluted to about 250 c. c. and sodium phosphate in excess added. If a precipitate forms, acid is added until it redissolves. Heat to boiling and then add sodium acetate until all the iron is precipitated as phosphate. To obtain very accurate results it is necessary to redissolve the precipitate and precipitate again in the same way. The nickel is precipitated from the filtrate as peroxide, by adding potassium hydroxide and bromine to the hot filtrate. The peroxide is dissolved on the filter with hot dilute sulphuric acid, the solution made alkaline with ammonia, and the nickel precipitated by the battery. A small quantity of ferric hydroxide will be found in the electrolyte but this has no influence on the results. If manganese and chromium are present the manganese is thrown down as peroxide on the anode while the chromium is oxidized into a chromic salt. No test analyses are given.

Volumetric Separation of Tin and Antimony. —H. Giraud, Bull. de la soc. chim., 46, 504. Trichloride of antimony is oxidized by iodine in a neutral solution. The reaction is complete and has been used for the volumetric determination of antimony. In an acid solution this reaction is no longer complete. When a large excess of acid is present the reverse action takes place, and iodine is separated from hydriodic acid as follows :



Bunsen has pointed out that this reaction may be used as a means of detecting traces of SbCl_3 in SbCl_5 . Stannic chloride is not reduced by the iodides under any circumstances. These facts may be made use of in estimating antimony in presence

of tin. The tin and antimony must be free from other metals, and in the state of chlorides. The liquid must be very acid to retain the antimony in solution. Potassium chlorate is added to form stannic and antimonie chlorides and the excess of chlorine driven off by heat. The solution is poured into a stoppered funnel tube, an equal volume of hydrochloric acid, an excess of potassium iodide and, finally, some carbon disulphide added, and the mixture agitated. After settling, the carbon disulphide, containing most of the iodine in solution, is drawn off through the stop cock and the shaking repeated with fresh quantities of carbon disulphide until it is no longer colored, this usually requires about 4 treatments. The carbon disulphide is then washed with water until neutral, and the iodine determined by means of a solution of sodium thio-sulphate of known strength. In drawing off the carbon disulphide, care must be taken that none of the solution goes with it, as this will carry off iodine during the washing. For this reason a funnel tube is selected in which the tubes soldered to the cock are of large size, and it is cleaned so that water wets it perfectly in all parts. In spite of this, however, a drop of solution is very apt to form at the bottom of the carbon disulphide.

If the antimony and tin have been separated as oxides with nitric acid, traces of copper will be found in the solution, which leads to error. Copper salts set free iodine and are reduced to the cuprous condition; on coming in contact with the air the cuprous oxidizes to cupric salt and liberates a fresh quantity of iodine. In spite of these sources of error the author has obtained good results. From 100 parts of pure antimony, the extreme results obtained were 99.8 and 100.8; with 100 parts antimony and varying amounts of tin, results within the same limits were obtained.

The author endeavored to use the oxidizing action of iodine upon stannous chloride in an acid solution, for the estimation of tin in presence of SbCl_3 , but without success.

Successive Separation of Copper, Cadmium, Zinc, and of Nickel or Cobalt, (Iron and Manganese).—M. Carnot, Bull. soc. chim., 46, 812.

Copper and Cadmium.—The solution containing the metals, acidified with 10 or 15 c. c. HCl, and diluted to about 200 or 300 c. c. is heated to boiling, and a solution of sodium thiosulphate is added in small quantities at a time, until the dark brown precipitate of copper sulphide ceases to form, and the solution becomes white and only sulphur is liberated by further addition of the reagent. Filter, wash, dry and burn, then calcine with powdered sulphur in an atmosphere of dry hydrogen in a Rose crucible; weigh as Cu_2S .

If cadmium alone remains in the solution it can be precipitated by sulphuretted hydrogen or by sulphide of ammonia.

Cadmium and Zinc.—Completely neutralize the HCl solution with ammonia, add an excess of sal ammoniac, and about 2 gms. oxalic acid (dissolved), then heat to boiling. Wash the crystals of oxalate of zinc by decantation with a hot solution of ammonium chloride until all cadmium is washed out. The zinc oxalate is added to the zinc sulphide separated further on.

To the filtrate add a little oxalate of potash and dilute to about 200 or 250 c. c. and heat to 100°C . Add sodium thiosulphate, in small quantities at a time, until no yellow precipitate is formed even on the addition of oxalic acid. Filter, wash, dissolve in nitric acid, evaporate to dryness in a crucible, take up with a few drops of sulphuric acid, then evaporate again, and burn and weigh as CdSO_4 which contains 58.54 per cent. of metal.

To precipitate the zinc, pass through the solution a rapid current of sulphuretted hydrogen, allow to stand in a dark place until the solution becomes clear. Filter, wash and add the oxalate of zinc previously separated, then convert into oxide by ignition, or into sulphide by ignition in sulphuretted hydrogen, and weigh.

Zinc and Nickel (or Cobalt).—If the solution contains nickel or cobalt, the metal would not be precipitated in any of the preceding operations. It is then necessary to add sodium or ammonium acetate and resaturate with sulphuretted hydrogen.

The operations become more simple when the solution contains no cadmium, as is usually the case with commercial alloys.

After having separated the copper add ammonia till the solution is only slightly acid; pass through a current of sulphuretted hydrogen, which will precipitate most of the zinc; the remainder of the zinc is precipitated by adding oxalate of ammonia and passing sulphuretted hydrogen through the solution. When the separation of the zinc is complete, the nickel or cobalt can be separated by adding a sufficient quantity of acetate of ammonia and again saturating with sulphuretted hydrogen.

Cobalt can be precipitated by the use of sulphhydrate of ammonia alone; for nickel it is necessary to use the sulphhydrate and acetate of ammonia, and finally acetic acid in excess and heat. In all these cases, the resulting sulphide of cobalt or nickel is ignited in a current of dry hydrogen and weighed.

If iron or manganese be present it is necessary to use oxalate of potash instead of oxalate of ammonia.

Zinc and Iron.—Pass through the hydrochloric acid solution, almost saturated with ammonia, a rapid current of sulphuretted hydrogen, add oxalate of potash, and then more sulphuretted hydrogen. Filter, and precipitate the iron from the filtrate.

Zinc and Manganese.—May be separated in exactly the same way as zinc and iron.

Zinc, Nickel, Manganese.—If the solution contain zinc, nickel or cobalt, and manganese at the same time, it is necessary to separate the three sulphides by working successively in an oxalic solution, acetic solution, and neutral or ammoniacal solution.

Nickel Iron and Manganese.—Saturate the solution with ammonia and with carbonate of ammonia until the liquid takes a brown color, then add a neutral solution of acetate of soda or ammonia and pass sulphuretted hydrogen; by this means iron, nickel and cobalt will be separated, and the manganese will remain in solution.

No test analyses are given.

W. D. O.

Analysis of Chrome Paints.—Walter Lee Brown, Sch. of Mines Quart., 8, 81; Chem. News, 54, 329. "The dry

chrome paints come on the market in several forms, as lemon chrome or chrome yellow, orange chrome, basic chromate of lead, and chrome green. They can also be procured ground.

1. *Analysis of Mixed Chromate and Sulphate of Lead* (lemon chrome or chrome yellow). — Pulverize the sample, pass through a 100-mesh sieve, and mix. To 1 gram in a small beaker, add HCl and heat. Any insoluble matter (usually barytes as a gross adulteration) is to be filtered out, washed, ignited, and weighed. Further, its weight is to be deducted from that of the total lead weighed as sulphate.

Lead.—1 gram is treated in a covered casserole with 25 c. c. concentrated H_2SO_4 , and heated moderately until the residue is perfectly white; cool, dilute, with 50 c. c. water, and again cool; add 50 to 75 c. c. of 94 per cent. alcohol, stir, and allow to stand one hour. Filter, wash with alcohol as usual, dry, heat, precipitate, and incinerate ash (after treatment with HNO_3 and H_2SO_4) $\frac{1}{2}$ hour, heat again 15 minutes, cool and weigh. The successive weighings should not vary more than .1 milligram.

The process ordinarily performed with HCl and alcohol does not, in our hands, give good results.

The $PbCl_2$ formed will stay neither entirely on the filter nor in the filtrate, and causes trouble all the way through. After repeated trials we had to give it up.

Chromium and Sulphuric Acid (SO_3).—Treat 1 gram with about 25 c. c. concentrated HCl, boil, dilute to 100 c. c., and while hot add excess of NH_4HO , which precipitates the chromium and the greater part of the lead. Boil off the excess of ammonia, filter and wash *very carefully* with hot water.

<i>Precipitate for Cr.</i> —Dissolve in dilute HCl, neutralize excess of acid with NH_4OH , precipitate Pb with H_2S gas and filter into a <i>porcelain dish</i> .		<i>Filtrate for SO_3.</i> —Acidify with HCl, concentrate, add boiling $BaCl_2$ drop by drop and determine SO_3 as usual, taking care to wash very thoroughly with hot water.
<i>Precipitate.</i> —	<i>Filtrate.</i> —Boil off every trace of H_2S and precipitate Cr with NH_4OH in the usual manner. Put the moist precipitate and filter paper into a crucible and ignite carefully. Weigh as Cr_2O_3 .	

Occasionally the following determinations are made :

Water—hygroscopic. Heat $\frac{1}{2}$ gram at 220° F. in air-bath, to constant weight.

Volatile Matter.—Heat 1 gram in a porcelain crucible to gentle redness; loss, less water, is volatile matter.

Water Extract.—(Acetates, sulphates, bichromates, or nitrates of soluble salts, indicating imperfect washing.) Treat 3 grams with 6 successive portions of 25 c. c. each, of cold distilled water, decanting and filtering each time, and evaporate the filtrate in a platinum dish to dryness on a water-bath.

* * * * *

2. *Analysis of Mixed Chromate, Sulphate and Carbonate of Lead* (lemon chrome and white lead).—Analysis made same as for 1—excess of lead is to be calculated as white lead, $2\text{PbCO}_3 + \text{PbH}_2\text{O}_2$. * * * * *

3. *Analysis of Orange Chromate of Lead* (chrome orange).—Process same as for 1. Very little PbSO_4 will usually be found. Closer results will generally be obtained from this paint, than from the mixed chromes. * * * *

4. *Analysis of Mixed Orange Chromate, Sulphate and Carbonate of Lead*.—Same as for 2. * * * *

Analysis of Red Chromate of Lead (known by many names, as scarlet, dark or basic chromate of lead, chrome red, Chinese red, red paste, American vermilion, and vermilion substitute).—Formula, $2\text{PbO}, \text{CrO}_3$, or Pb_2CrO_5 , or $\text{PbCrO}_4 + \text{PbO}$.

For the Pb determination take 1 gram in covered casserole, add 25 c. c. concentrated HNO_3 , heat to boiling, and *while boiling* add half a dozen drops, one at a time, of alcohol, by means of a pipette; boil a while longer, add water, and all of the chromate, if it is pure, will be found to be in solution. Without this alcohol treatment great difficulty will be experienced in getting the chromate into solution; with it, it becomes very easy. Add 25 c. c. concentrated H_2SO_4 , evaporate to white fumes and complete the analysis as described. For Cr and SO_3 determinations boil off alcohol and proceed as previously directed. * * * *

6. *Analysis of Chrome Green*.—Composed of Prussian blue

and yellow chromate of lead. The latter contains also sulphate of lead.

To 1 gram of the sample add 25 c. c. HCl, heat to boiling several minutes, add water allow to stand a while, then filter and wash thoroughly with hot water.

<i>Residue.</i> —Prussian blue (plus barytes or other insoluble matter if present). Dry and ignite to Fe_2O_3 . Weight multiplied by 2.212 equals per cent. Prussian blue. See Cr det.	<i>Filtrate.</i> —Nearly neutralize with NH_4HO , leaving, however, the solution slightly acid. Pass H_2S gas through till Pb is all precipitated. Filter and wash.	
	<i>Precipitate.</i> —PbS. Dissolve on filter with hot dilute HNO_3 (1.4) and boil solution. Filter from collected S and bring filtrate of $\text{Pb}(\text{NO}_3)_2$ to small bulk with several additions of H_2SO_4 . Evaporate to fumes of H_2SO_4 , cool, add water and alcohol, filter, wash and weigh as PbSO_4 as usual.	<i>Filtrate.</i> —For Cr (and Fe), boil off H_2S , add NH_4HO in slight excess, boil this off, and wash the $\text{Cr}_2(\text{OH})_6$ (and $\text{Fe}_2(\text{OH})_6$), as customary. Weigh precipitate as $\text{Cr}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. After the weight is obtained, mix with 1 part KNO_3 and three parts Na_2CO_3 , fuse in platinum crucible to clear fusion, cool, boil with water, filter and wash.
	<i>Residue.</i> —Filter, wash, dry, ignite and weigh as Fe_2O_3 , if it is wanted as a check.	<i>Filtrate.</i> —For Cr. Precipitate with NH_4HO in glazed porcelain dish as usual. If the weight of Cr_2O_3 is <i>very nearly</i> the same as before, then there has been no Fe extracted from the Prussian blue by the acid treatment. Some varieties are affected by this, others are not. If the weight is less than the original, deduct it from same, the result is Fe_2O_3 , which is also to be calculated to Prussian blue and added to the other.

Sulphuric Acid.—1 gram heated with 25 c. c. HCl, filtered from Prussian blue, and SO_2 in the filtrate determined as directed under 1. * * * * *

To determine the mixing fluid in any ground chromate, tare a small beaker and weigh into it from 10 to 15 grams of the paint. Stir the paint three times with naphtha, using about 25 c. c. each time, and withdrawing the mixing fluid solution by means of a small suction pipette, such as is used for filling stylographic pens, etc. Finally, treat once with ether, withdraw same, dry beaker and contents, and weigh; loss equals mixing fluid."

[As printed in the School of Mines Quarterly and the

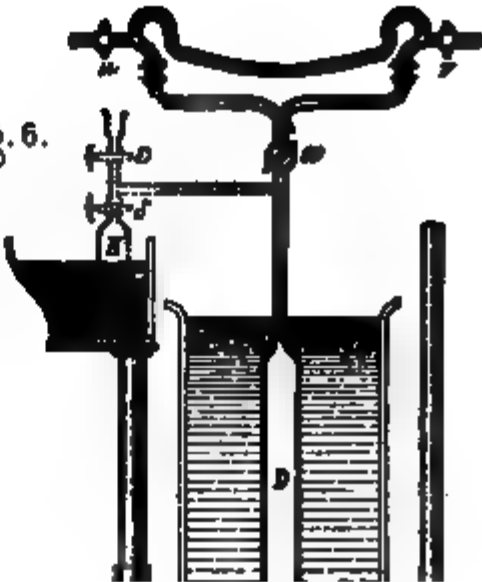
Chemical News, it is impossible to understand the meaning of some parts of the above article. It has, therefore been revised by the author, at our request, and is given here in its original and correct form, omitting only the calculations and examples. The author states that in the original publication the printers did not follow the arrangement of the Ms.—Ed.]

A New Principle of Eudiometry.—Otto Pettersson, Zeit. anal. Chem., **25**, 467. The apparatus shown in fig. 1 is intended for determinations of carbon dioxide and moisture in air. *A* is a pipette, the lower part of which is graduated. *B* is filled loosely with P_2O_5 and *C* with soda lime. The tubes which connect *C* and *B* with *A* are narrow but not capillary. They are drawn to a larger scale than the other parts of the apparatus for the sake of clearness. To make a determination *A* is filled with mercury by raising the reservoir at the side and then by lowering this reservoir and opening γ is filled with the air to be examined. The mercury is allowed to run out until it reaches about to the 0 mark. and then this is adjusted with precision by closing the stop-cock ϵ and turning the screw of the clamp f . The stop-cocks ϵ , δ and β are opened and the water around the apparatus stirred by means of the stirrers r r , fig. 1, *R* fig. 2, so that all the parts are subjected to the same temperature and pressure. The globule x now takes a position near the center of the scale which must be carefully noted through a microscope, since it must be brought back to exactly the same position before each successive reading of the volume of gas. γ δ β are now closed, the mercury reservoir raised until the gas all passes over into *B*, and the apparatus allowed to stand for 10–20 minutes until all moisture is removed from the gas which is then brought back into *A* and measured. As the air has been under pressure in *B*, it is necessary to allow it to stand a few minutes after it is brought back into *A* that it may regain the temperature of the surrounding water. After the volume of dry air remaining has been determined in the manner described below the air is transferred to *C* in the same way, the CO_2 removed and again measured in *A*. Ten minutes is sufficient time for

Fig. 2.

Fig. 6.

Fig. 4.



=



the absorption of all CO_2 , and if the soda-lime has been carefully dried the gas will not take up any moisture from it. After the moisture has been removed the volume decreases so much that the mercury rises into the wider part of the measuring tube, and it is best before determining the CO_2 to introduce an additional amount of air through μ . The method of measuring the volume of air left is the "New Principle" involved and allows the measuring of the volume of air remaining after each operation without reference to the changes of temperature or pressure. Variations in the pressure of the outside air are without influence since the stop-cocks δ and μ are closed during the analysis. By stirring, the temperature of the water surrounding the tubes is kept uniform, and although the temperature of the water changes constantly, the change is very slow and the pressure increases or diminishes alike in all three of the reservoirs. Two of these reservoirs, as A and B , communicate while C is shut off from them. After the air is brought back in A , the level of the mercury in the reservoir is so placed that the pressure is nearly the same as at the beginning. The tap γ is then closed, β opened and the screw f turned until the globule x takes exactly the same position as it had at the time the air in A was first measured. The same method is used in measuring the air after it has been forced into C . The globule x is sulphuric acid with a little dissolved indigo or, still better, high boiling petroleum.

If the difference of temperature from first to last does not amount to one degree it has no influence upon the result since the air and all parts of the apparatus expand and contract equally. When this is exceeded there is a small error due to the difference in the coefficients of expansion of soda-lime and phosphorus pentoxide. This error is not large but may amount to several parts in a million, of the total volume. As the apparatus has to withstand considerable pressure it is necessary that the stop-cocks be not too conical in shape and that they be very carefully ground.

A Method for Gas Analysis by the same author appears in the *Zeit. anal. Chem.*, **25**, 479. The apparatus above de-

scribed is so modified as to permit of the analysis of other gases than air, and other constituents than carbon dioxide and water may be determined. A front view of the modified apparatus is shown in fig. 5 and a rear view in fig. 6. The gas to be examined is collected in *K* over mercury, measured in *A* and the constituents to be determined, removed by transferring it to the absorbing vessels *B* and *C* containing appropriate solutions. As the figure shows, mixtures of oxygen and inflammable gases may be subjected to less than atmospheric pressure and exploded by a spark. As the measuring tube *A* is small (6.5 c. c.) it is necessary to read very carefully, and this is accomplished by fastening a milk glass scale upon the back of the tube and etching the same scale upon the face.

IRON AND STEEL.

EDITED BY P. W. SHIMER.

Determination of Phosphoric Acid in Thomas Slags.—E. Thilo, *Chemiker Zeitung*, February 16, 1887. The author carries out a rapid determination of phosphoric acid in Thomas slags by 1st, titrating the ammoniacal solution of the yellow precipitate instead of drying it. 2nd, omitting the separation of silica. 3rd, by using a relatively small excess of molybdate solution. Numerous determinations showed that the results were the same, whether the silica was separated or not. The method is as follows: 2 to 5 grms. of the finely ground slag are weighed into a measuring flask of such a size that, after solution and dilution, 50 c. c. shall contain $\frac{1}{4}$ gm. slag. While being shaken vigorously, 20–50 c. c. hydrochloric acid is added and brought to a boil. After complete solution, nitric acid is added and boiled till all protoxide of iron is oxidized. After cooling and dilution, 50 c. c. are removed into a beaker by means of a pipette, and precipitated by ammonia. Nitric acid in slight excess is then added, the solution is warmed to 70° C, and precipitated

by 50 c. c molybdate solution. The solution is well stirred, and in 5 minutes the precipitation is complete. The precipitate is filtered off and thoroughly washed with a 20 per cent. solution of ammonium nitrate. The precipitate with the filter is now thrown into the beaker in which the precipitation was made, and a measured volume of the standard ammonia solution is added.

This ammonia solution is of such a strength that 1 c. c. dissolves .0669 grm. of the molybdate precipitate, which amount corresponds to 1 per cent. P_2O_5 in $\frac{1}{4}$ grm. slag. Such a solution contains about 32 grms. NH_4OH in 1 liter. The standard sulphuric acid solution for titrating the excess of ammonia is so prepared that 1 c. c. just about neutralizes 1 c. c. of the ammonia solution. Litmus is used as an indicator. The strength of the ammonia solution is determined either by the use of a weighed amount of pure, dry molybdate precipitate, or by use of a determined amount of sodium phosphate.

By the first and more rapid method, a solution of sodium phosphate is precipitated by means of an excess of molybdate solution. The precipitate is well washed with water, and dried on a watch glass by heating for several hours to $100^\circ C$. 1.339 grms. of this precipitate, corresponding to 20 per cent. P_2O_5 when $\frac{1}{4}$ grm. slag is taken, is weighed into a beaker and 30 c. c. of the ammonia solution is added. After complete solution and the addition of litmus, the excess of ammonia is titrated by means of the sulphuric acid solution till the neutral reaction, or violet color appears. About 10 c. c. of the acid should be required for this purpose.

The molybdate solution used contains 1 part molybdic acid, 3 parts ammonia, 15 parts nitric acid.

Volumetric Determination of Manganese.—Rud. Schöffel and Ed. Donath, *Stahl und Eisen*, No. 1, 1887, p. 30. Also *Monatshefte für Chemie*, December 1886, p. 639. The authors dissolve 1 to 2 grms. of ferro-manganese, spiegeleisen or pig iron by boiling with hydrochloric acid, and after dilution and filtration, boil the solution with an excess of potassium chlorate until all chlorine is expelled.

The solution must contain all iron as peroxide, and it is therefore necessary to test a drop with potassium ferricyanide. The solution is now diluted to a determined volume, (commonly 200 to 300 c. c.) an aliquot part is removed to a beaker and neutralized with sodium carbonate, and a slight excess of specially prepared oxide of zinc is added.

In the meantime 200 to 300 c. c. distilled water with about 30 c. c. saturated zinc sulphate solution are brought to a boil and a measured volume of potassium permanganate solution is added. Into the nearly boiling solution, the contents of the beaker are poured and the whole again brought to a boil. The excess of permanganate is titrated by means of a solution of arsenious acid.

The volume of permanganate equivalent to the arsenious acid must be taken from the volume of permanganate solution originally added, and the difference, multiplied by the proper coefficient, gives the amount of manganese in the part of the solution used.

In the case of manganese ores, $\frac{1}{2}$ gm. is taken for analysis. As these ores are not usually completely soluble in hydrochloric acid, the insoluble residue is fused with sodium and potassium carbonates, and the fused mass dissolved in hydrochloric acid and added to the main solution.

Color Test for Carbon.—C. H. Ridsdale, F. C. S., The Journal of the Society of Chemical Industry No. 11, Vol. V, p. 585. The author describes a new form of apparatus for color tests, and gives notes on Stead's alkali method for the estimation of low percentages of carbon in iron and steel. The steels to be tested contained less than .09 carbon and sometimes as low as .02 per cent. The time taken for a determination was 35 to 40 minutes. The results are believed to be as accurate as those obtained by a carefully conducted combustion.

Mr. Stead's method, as published, is as follows: Dissolve 1 gm. of the sample in 12 c. c. nitric acid, of sp. gr. 1.20; heat to 90° or 100° C, till the sample is dissolved, which will take about 10 minutes. Then add 30 c. c. boiling water, and 13

c. c. sodium hydrate solution of sp. gr. 1.27; shake and make up to 60 c. c. for the test. The author adheres to this method except that he adds 18 c. c. caustic soda solution, lets rest 10 minutes after shaking, and then makes up to 70 c. c.

The apparatus devised by the author consists of the following parts (see illustration): "Three glass tubes of equal bore throughout. The centre one sealed at the bottom. Each of the outside ones is drawn out fine, and prolonged about three

inches, passing through an india rubber cork to within half an inch of the bottom of a bottle of ruby glass. On each of the tubes is loosely fitted a small cylinder, about one inch long, of glazed china clay or porcelain, or a sealed glass tube containing some heavy white powder, such as barium sulphate. Two syringes, one for each bottle, are connected therewith, either directly or with india rubber tubing, to a small piece of glass tube, which just passes through the cork. There is also

a third tube with a tap in it, which passes from the lowest point of the bottle, through the cork, and bends over for about two inches towards the back of the apparatus. Above the three comparison tubes is a mirror, which can be turned to any angle so as to enable the operator to see down them. On one side is a scale for measuring the height of the column of liquid in the tube, on the other a pointer which slides on a brass rod. A frame work of mahogany for the above, the whole of which *revolves* on a circular bottom weighted with lead. The apparatus can thus be instantaneously turned round for better comparison of color, without sacrificing its stability.

DIRECTIONS FOR USE.—Fill the centre tube up to 20 divisions with the liquid to be tested. The tubes on each side are for the standards, which may be of different depths of tint, thus enabling better comparison to be made than if only one standard is used.

To Fill with Standard.—Open the cock on the bent tube, stop the top of the comparison tube either with a cork or the finger, then hold a little beaker, containing the standard, so that the bent tube dips into it, and draw up the syringe, when the liquid will at once rush into the bottle.

To Make the Comparison.—Turn off the tap of the bent tube, remove the cork or finger from the comparison tube, and force the liquid up till the depth of tint, as shown by the mirror at the top, is equal to that of the 20 divisions of the liquid being tested. Read off the height of the column on the scale, calculate, *number of divisions of standard* \times *by percentage of standard* \div *by number of division of liquid being tested* = *the percentage*.

To Empty Out Old Standard.—Stop the top of the comparison tube, open the top of the blow-out tube and force the liquid out of the bottle by pressing down the syringe.

To Clean the Bottles Out.—When a new standard is to be used, it is better after emptying the bottle, to suck a little of the new standard in, and force it out again. If necessary, from time to time, the bottle can be cleaned out in the same way with dilute hydrochloric acid, and then water. * * * *

It was found that the standard, though not as sensitive to the action of light as in the ordinary color method, was still somewhat subject to change in the course of a day. The bottle for holding it was, therefore, made of ruby glass, and by thus excluding actinic rays, one standard may safely be used for 12 hours at least."

ASSAYING.

EDITED BY F. C. BLAKE.

Before undertaking to edit abstracts and articles on "Assaying," it would not be unwise to arrive at a definition of the word.—That there is a need for more general concurrence in a definite meaning of the verb *to assay* will be made evident by a few quotations. Mitchell in his "Manual of Practical Assaying" gives the following:—"ascertaining the richness in metal of any sample of ore." He "assays," however, for sulphur and to determine the heating power of fuel, and is in other ways inconsistent with his definition. Wm. Crookes in the Encyclopedia Britanica writes of Assaying:—"This term is used in metallurgy to denote a chemical operation in which the quantity of one ingredient of a mineral or alloy is determined; it is chiefly used in reference to the precious metals, gold and silver.

In the wider acceptation of the term in which it is used amongst practical metallurgists, assaying means almost the same thing as the quantitative estimation of one constituent of a compound, when the process adopted is one which has to be frequently repeated in a laboratory, and the results are required for commercial purposes."

Of this wider meaning the last clause is the only part that applies particularly to assaying. This definition is, however, much better than that in the valuable manual, "Notes on Assaying" by Prof. Ricketts:—"Assaying has for its object the determination and extraction of the metallic elements

from their various compounds'' and further dividing into ;
'' 'Dry way,' or assaying proper ; 'Wet way,' or analysis.'''

A still more incompressive definition is that in the ''Manual of Assaying'' by Walter Lee Brown, as follows: ''A comprehensive definition of assaying is to call it, that branch of exact science which enables us to find out of what a substance is composed and the proportions, by means of dry reagents and heat. On the other hand, analysis is that branch which effects the the same results mainly by the use of wet reagents, with or without the aid of heat. In spite of this distinction, *wet assays* as opposed to *dry* or *fire assays*, are continually spoken of ;'' Dr. R. W. Raymond in his ''Glossary of Mining and Metallurgical Term,'' defines ''assay'' thus: ''To test ores and minerals by chemical or blowpipe examination; said to be in *the dry way* when done by means of heat (as in a crucible), and in *the wet or humid way* when done by means of solution and precipitation or liquid tests. An assay differs from a complete analysis in being confined to the determination of certain ingredients, the rest not being determined. Both assays and analyses may be either qualitative or quantitative.''

Further examples of definitions could be readily given, but the above are ample for illustration. The use of the word *assay* is properly, I think, not limited to the determination of the proportion of ''metal'' in an ore ; nor is it necessarily confined to the determination of one element or ingredient of an ore, except as an assay is referred to as applying to a special determination (as the word *analysis* is likewise used.)

''Assaying proper'' is not necessarily ''dry'' and ''wetness'' is not an essential state of analysis.

Analysis is the more comprehensive word and may include much that is termed assaying. It is much easier, however, to shoot around definitions than directly at a correct meaning. An essential idea in the word *assay* is that it is a means to the *valuation* of the product assayed; and I would give the definition as follows: To assay is to determine in an ore or other product the amount of any ingredient upon which the commercial value of the ore or product is based. This definition

may seem too broad, but the common use of the term at the present time gives distinctively the meaning that *assaying* is a method to the valuation of the material assayed. The processes of *assaying* are not limited to either *dry* or *wet* methods or even to chemical reactions, for assays are made by mechanical or physical processes alone, though such methods are not frequently employed. We speak properly of the lead, copper, silver, zinc or iron assay of an ore because the market valuation is based upon these elements; distinctively the commercial valuation. We do not speak of assaying a lead ore for lime, though the amount of lime present affects its actual value because the amount of lime present in the ore is not made an element of commercial valuation. And under this meaning, it is hoped that much of definite value can be collected bearing upon the analytical processes used for the valuation of ores and other products which are bought and sold. Especial attention will be given to securing articles upon or promoting the uniformity of methods of assaying and the study of causes tending to produce inaccurate results in assaying. Although mechanical, physical and chemical methods are allowed, mental processes of assaying are expressly excluded.

Determination and Valuation of Copper in Ores and Products for Commercial Purposes.—James W. Westmoreland, Jour. Soc. Chem. Ind., V, 48, has published a valuable review of methods of copper assay in common use; the paper being suggested by a discussion before the Society of Chemical Industry upon "Uniform Methods of Analysis." The paper should be read by all chemists who make copper assays, but it is too long for full abstraction. The writer details and criticizes the processes used for the estimation of moisture, copper by wet and dry methods, comparing results with an improved method. The author personally uses E. O. Browns' iodide method and that of electro-deposition, especially recommending the former.

MINERAL ANALYSIS.

EDITED BY JOHN EYERMAN.

Fayalite from Yellowstone Park.—F. A. Gooch (Bull. 27, U. S. Geol. Sur.) gives analysis of Fayalite.

10.36 per cent. of material insoluble in HCl.

SiO ₂ (in insoluble part)	7.02
SiO ₂ (in soluble part)	25.61
Fe ₂ O ₃	14.92
FeO	51.75
Al ₂ O ₃	tr.
MgO	1.66
CaO	none.
Ignition	none.
	<hr/>
	100.96

Serpentine from Newburyport, Mass.—F. W. Clarke (Bull. 27, U. S. Geol. Sur., pp. 63).

H ₂ O	SiO ₂	FeO	MgO	Total.
14.54	41.32	2.36	41.49	99.71

Rhyolite from Washoe, Nevada.—F. A. Gooch (Bull. 27 U. S. Geol. Sur. pp. 66)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	ign.	Total
73.07	11.78	2.30	2.02	0.39	1.19	6.84	2.24	99.83

Meteoric Iron from Mazapil, Mexico.—W. E. Hidden (Amer. Jour. Sci., March 1887) describes a meteorite which fell at Mazapil, Mexico, November 27, 1885. An analysis by J. B. Mackintosh resulted

Iron	91.26
Nickel	7.845
Cobalt	0.653
Phosphorus	0.30
	<hr/>
	100.058

Nickeliferous Metallic Iron from New Zealand.—G. H. F. Ulrich describes in a letter to the editors (Amer. Jour. Sci.,

March 1887, pp. 244) a nickeliferous iron from the drift of Gorge River, New Zealand. Analysis by W. Skey afforded

Ni	67.63
Fe	31.02
Co	0.70
S	0.22
SiO ₂	0.43
	<hr/>
	100.00

Specific gravity—8.1. Hardness about 5.

Formula—Ni₂Fe.

The name *Awarvite* has been proposed by Mr. Skey.

Dacite from Washoe, Nevada.—F. A. Gooch (Bull. 27, U. S. Geol. Sur., pp. 65) gives anaylsis of Dacite from McClellan Peak, Washoe, Nev.

SiO ₂	69.96
Al ₂ O ₃	15.79
Fe ₂ O ₃	2.50
CaO	1.73
MgO	0.64
Na ₂ O	3.80
K ₂ O	4.12
Ign.	1.53
	<hr/>
	100.07

Goslarite from Montana.—R. Pearce (Proc. Colo. Sci. Soc. II, Part I, 12) describes goslarite from Butte City, Montana. An analysis by W. F. Hillebrand.

SO ₃	28.09
ZnO	27.56 (diff.)
CuO	0.12
MnO, FeO	0.30
H ₂ O	43.93
	<hr/>
	100.00

Allanite from Douglass Co., Col.—L. G. Eakins (Proc. Col. Sci. Soc. II, part I, 32) describes allanite from Douglass Co., Col. Analysis afforded

SiO ₂	31.13	CaO	9.44
Al ₂ O ₃	11.44	MgO	0.16
Fe ₂ O ₃	6.24	K ₂ O	tr.
Ce ₂ O ₃	12.50	Na ₂ O	0.56
(LaDi) ₂ O ₃	10.98	H ₂ O	2.78
FeO	13.59	CO ₂	0.21
BeO	0.27	P ₂ O ₅	tr.
MnO	0.61		
			<hr/> 99.91

A New Variety of Kobellite.—H. F. and H. A. Keller (Jour. Amer. Chem. Soc., 7, 7) give analyses of a variety of Kobellite from Leadville, Colorado.

S	15.21	15.27	15.19
Bi	32.62	33.31	33.89
Pb	43.94	44.28	44.03
Ag	5.78	5.49	5.72
Cu	trace.	0.03	trace.
Gangue	0.15	0.14	0.17
	<hr/> 97.70	<hr/> 98.52	<hr/> 99.00

Columbite from Colorado.—W. P. Headden has analyzed columbite from Turkey Creek, Jefferson Co., Colorado, which afforded

Nb ₂ O ₅	77.83
W ₂ O ₅ }	1.00
SnO ₂ }	
FeO	9.92
MnO	11.23
MgO	trace.
	<hr/> 99.98

Specific gravity, 5.48.

Manganese Zinc Serpentine from Franklin, N. J.—Geo. A. Koenig (Proc. Acad. Natl. Sci., III., 1886), has analyzed

a “very peculiar willemite” which has been proven to be manganese zinc serpentine. Analysis afforded

SiO ₂	41.70
MgO	29.24
MnO	6.91
ZnO	3.10
H ₂ O	14.04
Franklinite	4.15
Pyroxene	1.02
	<hr/>
	100.16

Hydrogiobertite.—E. Scacchi (Rend. R. Accad. Napoli, Dec. 1885,) gives a description and an analysis of this mineral from near Pollena.

Specific gravity, 2.149—2.174.

MgO	44.91
CO ₂	25.16
H ₂ O	29.93

Formula, 2 MgO, CO₂ 3H₂O.

Kainosite from Norway.—A. E. Nordenskiöld (Geol. Före. Förh. 8, pp. 143, 1885,) describes kainosite rare) from the pegmatites of Hitterö, Norway.

Specific gravity, 3.413. Hardness, 5.5.

SiO ₂	34.63
Y ₂ O ₃ }	37.67
Er ₂ O ₃ }	
Ce ₂ O ₃	traces
CaO	15.95
MgO	0.03
FeO	0.26
Na ₂ O	0.40
CO ₂	5.90
H ₂ O	5.29
	<hr/>
	100.13

Pinnoite from Stassfurth.—Staute (Ber. d. deut. chem. Ges., XVII, July 1884) gives the formula of pinnoite as

$\text{MgB}_2\text{O}_4 + 3\text{H}_2\text{O}$.

Specific gravity, 2.27.

Hardness, 3-4.

Polyarsenite, a New Mineral.—L. J. Igelström (K. Sv. Vet. Acad. Handl. Ofversigt, 1885, 7) describes a new mineral from Sjögrufvan Kirchspiel Grythyttä, Amtsbezirk Orebro which he has named polyarsenite.

Specific gravity, 4.085.

Analysis by H. G. Söderbaum gave

H_2O	[3.15]	[3.15]
CO_2	[3.51]	[3.51]
As_2O_5	39.23	38.86
Sb_2O_5	1.37	1.04
MnO	49.88	50.47
FeO	trace	trace
CaO	2.85	2.92
MgO	0.77	0.73
	<hr/> 100.76	<hr/> 100.68

Formula, $(\text{MnO})_4 \text{As}_2\text{O}_5 + \text{H}_2\text{O}$.

Richellite from Visé, Belgium.—G. Césaro and G. Despret (Ann. de la Soc. Géol. de Belgique, X, Mémoires, 1883,) describe and give analyses of this mineral.

Specific gravity, 2.

Hardness, 2-3.

Formula, $4 \text{Fe}_2 (\text{PO}_4)_3 + \text{Fe}_2\text{O}_3, \text{HFl} + 36 \text{H}_2\text{O}$.

Koninckite.—G. Césaro (Ann. de la Soc. géol. de Belgique, XI, pp. 247,) gives the formula of this mineral as

$\text{P}_2\text{O}_5, \text{Fe}_2\text{O}_3 + 6 \text{H}_2\text{O}$.

Specific gravity, 2.3.

Hardness, 3.5.

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Silver and Copper.—Shaw (Phil. Mag. (5) 23, 138,) has de-

terminated the ratio between these metals electrolytically. If the equivalent of copper be taken as unity, that of silver becomes 339.983. Hence, if $\text{Ag}=107.675$, $\text{Cu}=63.338$. Shaw points out that the ratio of Ag to Cu is almost exactly 17:10, and that the same ratio connects K with Na.

Gold.—Krüss (Ber. der deut. chem. Ges., 20, 205) has published an abstract of a forthcoming memoir on the atomic weight of gold. Five ratios were established, representing thirty experiments; but only mean values are given. They may be summarized as follows:

1. Analysis of neutral AuCl_3 solution. The gold, reduced by sulphurous acid, was weighed as metal, and the chlorine was weighed as chloride of silver. Eight experiments gave in mean the value $\text{Au}=196.622$.

2. Nine determinations of gold in KAuBr_4 gave in mean $\text{Au}=196.741$.

3. In five analyses of KAuBr_4 the bromine was also determined as silver bromide. Hence we have the ratio $4\text{AgBr}:\text{Au}$; from which the value $\text{Au}=196.743$ was deduced.

4. In four analyses of KAuBr_4 the salt was reduced by heating in hydrogen. The loss in weight was Br_2 , and the values obtained for the ratio $\text{Br}_2:\text{Au}$, gave $\text{Au}=196.619$.

5. In the preceding four analyses, after ignition, the residual KBr was extracted with hot water and weighed. Hence the ratio $\text{KBr}:\text{Au}$, which gave $\text{Au}=196.697$.

In mean, the thirty experiments gave a final value of $\text{Au}=196.669$; Stas' figures for Ag, Cl, K, and Br being apparently taken, with hydrogen as unity.

AGRICULTURAL ANALYSIS.

EDITED BY H. W. WILEY.

Estimation of Ammonia-Nitrogen in Soil.—The discussion of the methods of estimating ammonia in soils has, during

the past year, been carried on quite extensively by agricultural chemists.

Schlösing and Berthelot have contributed several articles to the "Comptes Rendus" on this theme, a resumé of which will be given further on.

Bauman¹ has reviewed the different methods and shown the inaccuracies to which they may lead. Bauman makes the curious mistake of attributing the following method to Schlösing:

The method consists in treating the soil (50 gms.) with 50 c. c. soda-lye (one part NaOH and two parts H₂O) in the cold for three days. The H₂N is absorbed by $\frac{1}{4}$ normal H₂SO₄ contained in small porcelain dishes. The whole experiment is made under a jar separated from the air by being sealed with mercury.

Boussingault's method consisted in replacing the soda-lye with magnesia and distilling off the ammonia, which is absorbed by standard acid.

This process was soon modified, however, by using a hydrochloric acid extract of the soil instead of the soil itself in the distilling flask.

According to Bauman the absorbed ammonia should not be estimated by titration but by conversion into free nitrogen.

If asparagin or glutamin be present, they are decomposed by the soda-lye and the results obtained are too high.

By a series of experiments Bauman has shown:

1. Soils containing humus, give with soda-lye in the cold, a continuous evolution of ammonia.

2. Soils rich in humus, previously boiled with calcined magnesia, give on treatment with soda-lye considerable additional quantities of ammonia, but humus free soils none.

3. For the reasons given above, soils rich in humus cannot be treated by Schlösing's method for ammonia.

Knop's method is also discussed by Bauman. In this method the soil is treated in a closed cylinder with soda-lye containing bromine. The ammonia set free by the lye is decomposed at once in presence of the bromine into free nitro-

1. Versuchs-Stationen, Vol. 33, pp. 247-303.

gen and hydrochloric acid. The nitrogen is collected and measured in Knop's azotometer. The brom-soda-lye is prepared by dissolving 100gms. NaOH in 1250 c.c. H_2O and adding 25 c. c. Br. The decomposition takes place in a few minutes.

A careful trial of the method has convinced Bauman that it is unreliable. These experiments show that results obtained give no accurate idea of the actual content of ammonia in the soil. The use of borax solution in the brom-soda-lye is shown to be without any signification. Knop originally used it to diminish the alkalinity of the mixture, but it really increases it.

In general it is shown that the use of Knop's azotometric process for estimating ammonia in soils is absolutely unreliable even when supplemented with the borax solution.

A radical modification of the process proposed by Bauman is as follows :

200gms. soil is treated with 100 c. c. ammonia free HCl (1 part HCl and 4 parts H_2O); 300 c. c. ammonia free distilled water added and the whole digested for two hours with frequent stirring.

If the soil contain much $CaCO_3$ it may be necessary to use a larger quantity of acid than that mentioned. A too great rise of temperature in such a reaction must be avoided by keeping the vessel containing the mixture cold.

200 c. c. of the filtrate (corresponding to 100 gms. soil) are placed in the evolution flask of the azotometer and 5 gms. freshly burned magnesia added. The mixture is then oxidized by ozone in the following manner. Ozone is generated by adding 3 parts by weight H_2SO_4 to one part of dry and powdered permanganate of potassium. A stream of air is drawn through this mixture by an aspirator and the ozone is conducted into the flask containing the hydrochloric acid extract of the soil treated with magnesia. The oxidation is completed in 10 minutes.

The mixture is then brought into the evolution flask of the azotometer and the nitrogen set free and measured in the usual way.

The author thinks this a promising method, but is not quite

prepared to recommend it over methods of Schlösing and Boussingault.

NOTE.—It will be instructive in connection with the above abstracts of recent literature relating to ammonia in the soil, to call attention to the discussion which was carried on last summer in *Comptes Rendus*, on this subject by MM. Schlösing, Berthelot and André. Vol. 102, Nos. 17, 18, 20, 22, 23, 24, 25 and Vol. 103, Nos. 2, 3, 4 and 5.

Berthelot and André advised that the estimation of the ammonia in the soils ought to be made without previous desiccation. The method of estimating the ammonia was by contact with soda-lye in the cold; a process ascribed to Schlösing.

Commenting on this paper M. Schlösing said:

“I am indeed the author of a process for determining ammonia by treatment in a confined space in presence of standardized sulphuric acid, but I have not applied this process to earth containing vegetable matter. Still less have I recommended the use of concentrated soda-lye for this purpose. This application does not belong to me and I do not desire that it should be attributed to me.”

This is certainly plain enough and shows that what is generally regarded as “Schlösing’s Process” for determining ammonia in vegetable mold, or soils containing it, should be credited to some one else.

Schlössing also objects to the conclusions of Berthelot and André to the effect that such soils tend to give off ammonia, contending on the other hand that they are rather disposed to absorb it from the air.

M. Schlösing describes further four methods of estimating ammonia which he used in examining certain soils from Boulogne and Neauphle :

1. Estimation of ammonia by the process of Boussingault (boiling with magnesia).
2. Estimation of the ammonia by the above process modified by Schlösing in Vol. X of “*Fremy’s Encyclopédie Chimique*.”
3. Estimation of the ammonia in 100 gms. soil, treated for 48 hours in a closed vessel in presence of titrated dilute H_2SO_4 by

hydrate of lime (3 gms. lime, previously heated to redness, and then mixed with 30 c. c. water).

The author says, "This is a method which I described several years ago, but I have been careful not to apply it to soils containing vegetable mold."

4. Estimation of ammonia as above, replacing the milk of lime by a solution of caustic soda, deprived of ammonia by previous boiling.

Schlösing disclaims the above method for himself, but does not say who is the author of it. [As will be seen presently it is the method of Berthelot and André.]

By the use of method No. 4 from 14 to 24 times more ammonia was obtained than was yielded by the process of Bous-singault.

Schlösing also thinks that by drying the soil and thus suspending the action of nitrifying ferments, it is possible to get a much better idea of the real quantity of ammonia present than by neglecting the desiccation as Berthelot and André recommend.

Berthelot and André after discussing the various methods of estimating ammonia describe their own process. It consists in treating the soil in the cold with an alkali which displaces the ammonia. These chemists use a solution of NaOH containing 50 to 80 gms. of the alkali per litre. In each case 25 to 50 gms. of soil are treated, as soon as possible after the sample is taken, with the soda solution in a closed vessel, the ammonia being absorbed by dilute H_2SO_4 of known strength. The time employed is 48 hours.

They say: "we had thought it was just to attribute this process to M. Schlösing whom we regarded as its inventor. We take notice of his reclamation; we will beg of him to apply our proceeding to the soils he has studied."

M. Schlösing answered the above letter by giving the results of some experiments which show that the amount of ammonia obtained by the process of Berthelot, is enormously greater than that given by distillation with magnesia, and increases moreover with the strength of the soda solution employed.

Solutions were used containing 14.5; 36.4; and 72.8 gms. NaOH per litre; 35 c. c. being used for each 100 gms. of soil.

The results obtained were as follows:

	Per kilo of soil.
Solution No. 1	11.3 mg.
Solution No. 2	40.5 mg.
Solution No. 3	75.7 mg.
Magnesia method	8.1 mg.

To which Berthelot and André reply : "In place of justifying his processes, M. Schlösing confines himself to attacking the employment of alkalis and to showing that they give results too high. We are far from denying the gravity of his objections, for it is necessary to speak in perfect good faith when we are together seeking the truth." It is also seen from the experiments published by the authors that the double salts of ammonia yield their ammonia very slowly even in presence of sodium hydrate. They show further that magnesia, under ordinary conditions of analysis, is incapable of displacing all the ammonia from its compounds.

To this M. Schlösing replied by giving the details of experiments, showing that by distillation with magnesia in his apparatus all the ammonia was obtained, and that even in the case of ammonio-magnesia-phosphate the ammonia was nearly all obtained in the distillate when boiled with milk of lime.

In all these experiments it is necessary to remember the fact connected with the titration of the standard acid that carbonic acid is not retained by magnesia as it is by the alkalis and lime. This acid may, therefore, be carried over and absorbed with the ammonia in the dilute H_2SO_4 . Before titration the acid must be boiled to get rid of CO_2 . [From the foregoing it is seen that the whole subject of estimating ammonia in the soil is still a question unsettled. There seems to be no other process connected with agricultural analysis on which there is such an unanimity of disagreement.]

Ammoniacal and Amide Nitrogen in Arable Soils.—Berthelot and André (Comptes Rendus, Vol. 103, pp. 1101

et seq.) describe a new method of distinguishing between ammoniac-nitrogen and amide nitrogen in arable soils.

The soils were taken from the experimental station of Meudon and after drying in the air 48 hours were passed through a sieve of one mm. mesh.

From 200 to 500 gms. were treated in a flask with water and HCl of different degrees of concentration and for varying lengths of time. The clear liquid was then poured on a filter and the residue washed by decantation until the total volume obtained was 1200 to 1400 c. c.

Neutrality was established with KOH and then the solution made slightly acid. From two to four grammes of recently burned MgO are added and the ammonia is determined by the Schlösing process. The ammonia pre-existing in the solution as well as that formed during the hour of boiling are thus obtained together.

After an hour's boiling the contents of the flask are neutralized by H_2SO_4 and evaporated to dryness on a sand bath. The combustion was then made with soda lime. The nitrogen obtained is derived from the soluble amides in the soil.

Analysis No. 1.

Weight of soil	-	-	-	137. gms.
Total nitrogen	-	-	-	1.744 gms.
Nitrogen from nitrates	-	-	-	.0035 gms.

No. 2. 500 gms. of the above soil in contact with one litre pure water for 18 hours, afterwards boiled with MgO as described above per kilogramme:

Ammoniacal nitrogen	-	-	.0017 gms.
Soluble amide nitrogen	-	-	.0083 gms.

No. 3. The same only with 200 gms. soil, 400 H_2O and 10 c. c. HCl (3.5 gms) :

Ammoniacal nitrogen	-	-	.0048 gms.
Soluble amide nitrogen	-	-	.02775 "

No 4. The same with 50 c. c. HCl :

Ammoniacal nitrogen	-	-	.0144 gms.
Soluble amide nitrogen	-	-	.0606 "

No. 5. The same with 100 c. c. HCl :

Ammoniacal nitrogen	-	-	-	.0149 gms.
Soluble amide nitrogen	-	-	-	.0686 "

It is seen from the above experiments that the quantity of ammonia furnished by a soil increases with the quantity of HCl employed.

The amides rendered soluble by HCl are divided into two groups ; one group remains in solution when the acid is neutralized by potash, the other is precipitated ; also with lime, alumina and ferric oxide.

Observed facts show that the ammonia furnished by a soil is derived almost wholly from a decomposition of the amides present, a decomposition that takes place in the presence of hot water even, but more rapidly with alkalis.

Rain water also contains certain amide principles, both soluble and insoluble, derived from atmospheric dust.

Quantity of Nitrogen as Ammonia in Soils. — Bauman (loc. cit.) has determined the ammonia-nitrogen in various soils by the soda-lye method ; distillation of the hydrochloric acid extract with magnesia, and the azotometric method modified as indicated. These methods will be designated as 1, 2, 3, in the following table.

No. of Sample.	METHOD.		
	1	2	3
	Ammonia-nitrogen in 1 kg. of soil.		
1	.0448 gms.	.02227 gms.	.02781 gms.
2	.0168 "	.01105 "	.01326 "
3	.0336 "	.01771 "	.02214 "
4	.0056 "	.00443 "	.00443 "
5	.0280 "	.02337 "	.02894 "
6	.0196 "	.01243 "	.01672 "

(From the above figures it is seen that the method usually attributed to Schlösing gives uniformly higher numbers than either of the other processes, while the third gives slightly higher values than the second.)

Estimation of Fluorine in Phosphates. — A Chapman, Chem. News, 54, 287. This method, originally devised by Dr.

Graham, of the Birbeck Laboratory, University College, depends upon the fact that a solution of ammonium acetate containing free acetic acid precipitates calcium fluoride, but not calcium phosphate, from their solution in acids. 2.5 gms. are ignited in a platinum crucible for a short time (this ignition prevents ferric and aluminum phosphates from dissolving in dilute hydrochloric acid), transferred to a mortar and ground up with repeated small quantities of ten per cent. hydrochloric acid, filtered and washed.

The filtrate is made up to 250 c. c. 100 c. c. taken, and to it the ammonium acetate added; calcium fluoride precipitates and is filtered off, dried, ignited and weighed. If the phosphate is not first ignited the calcium fluoride is contaminated with phosphates of iron and aluminum. No test analyses are given. H.

TOXICOLOGY.

EDITED BY V. C. VAUGHAN.

Contributions to Toxicology.—*Detection of Chloral.**—Dragendorff recommends the following method for the detection of chloral in organic mixtures, such as the contents of the stomach. Acidulate the mixture with dilute sulphuric acid, then macerate with three volumes of strong alcohol for 24 hours, allow the alcohol to evaporate spontaneously, then extract the aqueous residue with petroleum benzine to remove the fat, and subsequently with ether, which removes the chloral. From the blood, chloral may be obtained in the form of chloroform by distillation with sodium hydrate. After the separation of the chloral it is best identified by the following tests: Warmed with an alcoholic solution of sodium hydrate and a little pure analin, chloral gives off the odor of isonitril. Heated to 50° with a few drops of an aqueous solution of potassium hydrate and a little naphthol, a blue coloration is obtained. The urochloralic acid in which form chloral is, in part at least, excreted in the urine, does not give the reactions of chloral.

*See page 117 of this Journal.

Detection of Phenol.—For the detection of phenol he proceeds as follows: Macerate the mixture with four volumes of alcohol for 24 hours ; from the filtrate remove the alcohol by distillation at a low temperature and under reduced pressure ; filter the aqueous residue, agitate with petroleum benzine to remove the fat, then shake repeatedly with benzol and evaporate the benzol in watch-glasses. To the residue the following tests may be applied: left in contact with solution of mercuric nitrate containing a little nitrous acid, a red color appears within half an hour, if there was one part of phenol to 100,000 of the mixture.—Dragendorff's test.

Or dissolve 3 drops of colorless analin in 50 c. c. of water. Dilute 5 to 10 drops of this solution with 5 c. c. of water, and add sufficient sodium hypochlorite to produce a distinct violet or brown color. Add enough of this freshly prepared mixture to the suspected substances, made alkaline with ammonia, until the whole is colored violet or brown. If phenol be present in quantity of 1 to 50,000 the color will in a short time become blue, or with less phenol, green.—Jacquemin's test.

Or dissolve a bit of the suspected matter after extraction with benzol, in water, and expose to the vapor of bromine. If phenol be present, an amorphous precipitate will be obtained, and this, after solution in alcohol and spontaneous evaporation of the alcohol, forms in needle-shaped crystals.—Landlot's test.

Detection of Thalline.—From ammoniacal solution, thalline is removed by agitation with benzine, benzol, chloroform and ether. Thus extracted and dissolved in water, thalline gives with ferric chloride a green color.

A like color is also produced by gold chloride, silver nitrate, chromic acid, chlorine water and mercuric nitrate. Iodine produces a dark brown, changing into green, and platinum chloride, a yellowish-green.

Detection of Antipyrin.—Treat the aqueous infusion of the suspected matter, rendered alkaline with ammonia, with benzol, chloroform or amylic alcohol. The alkaloid thus ex-

tracted is precipitated from neutral solution by ferric chloride, a dark-brown to yellow color. Fuming nitric acid colors dry antipyrin dark red, and added to a solution of the alkaloid gives a green. Concentrated sulphuric acid with a little fuming nitric acid warmed with a solution of the alkaloid gives a deep red.—*Parmaceutische Zeitschrift für Russland*.

Researches on Ptomains.—Brieger has obtained from the cadaver the following ptomains: Cadaverin ($C_6H_{14}N_2$), putrescin ($C_4H_{12}N_2$), a base similar to curare in its action and called mydatoxin ($C_6H_{13}NO_2$) and mydin ($C_8H_{11}NO$). From the flesh of the horse he found cadaverin, putrescin, a feebly acid, toxic substance of the composition $C_7H_{17}NO_2$, mydatoxin and methylguanidin ($C_2H_7N_2$). In putrid fish he found cadaverin, putrescin, methylamin, dimethylamin, trimethylamin, diethylamin and neuridin ($C_8H_{14}N_2$). From poisonous muscle he has obtained mytilotoxin ($C_6H_{13}NO_2$), which produces curare-like symptoms, also a non-poisonous base, betain ($C_5H_{11}NO_2$). From cultures of the Eberth typhoid bacillus Brieger separated typhotoxin ($C_7H_{17}NO_2$). This ptomain produces in the lower animals lethargy or stupor and diarrhoea. With cultures of the tetanus germ (of Flügge, Nicolaier and Rosenbach) was formed a base ($C_{18}H_{30}N_2O_4$), which produces the same symptoms as inoculations with the germs do.—*Untersuchungen über Ptomaine, Dritter Theil*.

On Ptomains in Toxicology.—Prof. Marino-Zucco embodies his researches on ptomains in the report of the Royal Italian Commission for the ascertaining of specific tests in cases of poisoning. (*Relazione delle Esperienze fatte nel Laboratorio della Commissione sulle così dette Ptomaine*. Roma, Ripamonti, 1885.) He obtained from fresh eggs, blood, brains, liver, etc., by the method of Stas as well as that of Dragendorff, relevant quantities of a base which gave alkaloidal reactions and on analysis was found to be neurine. He proved that this base did not pre-exist in the organs, but was formed by the action of acids upon the lecithin contained in them, and not from the albuminoids present. Neurine can mask the re-

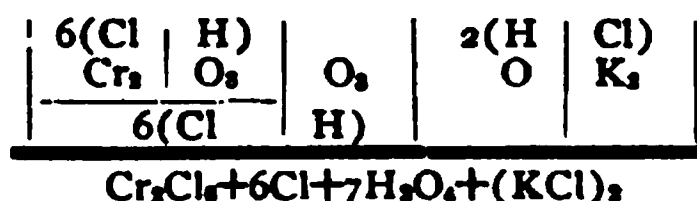
actions of vegetable alkaloids, such as strichnine, and hence it is necessary to separate it before making the usual tests. This is done by taking up the extract, obtained by either method, in acidulated water, re-precipitating with NaHCO_3 or NH_4OH and extracting again with ether or chloroform. Neurine is insoluble in the solvents, and by repeating the operation several times may thus be completely removed from any vegetable alkaloids that may be present. Larger quantities of neurine are obtained by Dragendorff's method than by that of Stas, but this is not due to a difference in the action of the acids employed, but is dependent upon the amount of extractive matter in which the neurine is soluble. This amount is much greater with the former method than with the latter.

From the liver and spleen he obtained in addition to neurine another base, the hydrochloric solution of which exhibited a beautiful violet fluorescence, similar to that of the salts of quinine. Unlike neurine it is soluble in the reagents employed. The fluorescence increased on the addition of H_2SO_4 . With general reagents it behaved the same as quinine, but did not give the characteristic green coloration produced by quinine on addition of chlorine water and NH_4OH , and instead gave a white precipitate. This substance is the same as the "Animal Chinoidin" discovered by Bence Jones and Duprè.

Experiments made on various organs of decomposing cadavers, yielded a base which was apparently the same from all, and from its behavior to solvents appeared to be neurine. Minute traces of other alkaloids were obtained. Under the conditions that a toxicologist works, these cadaveric alkaloids are not found in appreciable quantity and can be separated from vegetable alkaloids by the method given above.

NOTES.

—Dr. W. V. Miller, Ordentlich Professor and Dr. H. Killiani, Privatdocent, in the Royal Technical School at Munich, have issued a "Kurzes Lehrbuch der analytischen Chemie," in which they have introduced a new system of writing reactions. The action of hydrochloric acid upon potassium dichromate ordinarily written $K_2Cr_2O_7 + 14HCl = Cr_2Cl_3 + 2KCl + 7H_2O + 3Cl_2$ is thus expressed according to the new plan.



—Miss Helen C. De S. Abbott has just concluded a course of lectures on "Plant Analysis as an Applied Science," at the Franklin Institute, Philadelphia.

—Prof. H. C. Bolton, of Trinity College, has undertaken to keep the readers of the JOURNAL informed of the new books issued of especial interest to analytical chemists. This number contains a list of Chemical Periodicals. No. 3 will contain a list of works on Analytical Chemistry issued during 1886 and No. 4 a list of those issued during 1887.

—The annual address before the Chemical Society of Washington, was delivered on Dec. 9, '86, by the President, Prof. H. W. Wiley, subject, "Our Sugar Supply." The address is full of meat and any one, scientific or unscientific, can read it with pleasure.

—Gmelin-Kraut's Handbuch der anorganischen Chemie still drags its slow length along. Pages 785-928 of Vol. 2, Part I, have just appeared. This is a very valuable work but has been issued at such a leisurely pace that part of it seems too much like ancient history. The title page of Vol. 1, Part 2, bears the date 1872; that of Vol. 3, 1875, and that of Vol. 1, Part 1, 1877.

—Bulletin No. 11, of the Wisconsin Agricultural Experiment Station, has just been issued, containing the Report on Wheat, Oats, Barley, Potatoes and Corn for 1886.

—BOOKS RECEIVED.—"Notes of Work by Students of Practical Chemistry in the Laboratory of the University of Virginia, No. XV. Communicated by F. P. Dunnington. Reprinted from the American Chemical Journal."—"Report of the Chemist to the New York Agricultural Experiment Station, by S. M. Babcock."—"Report of the Assistant Chemist to the New York Agricultural Experiment Station, by E. F. Ladd."—"The New Chemical Laboratory at the Missouri School of Mines, Rolla, Mo., by Chas. E. Wait."—"Bulletin of the United States Geological Survey, No. 32. Mineral Springs of the United States."—"Mineral Waters, by A. C. Peale. Abstract from Mineral Resources of the United States, 1885."

—Vol. III, No. I, of Dr. Squibb's "Ephemeris" has just appeared. Among the contents, the following are of interest to analysts, "Hydrochlorate of Cocaine," "Testing Aconitine" and "The Alcohol Question before Congress." Vols. 1 and 2 can now be obtained for \$1.16 each.

NEKROLOGY.—On Feb. 20, Carl Birnbaum, Professor of Chemistry in the Technical High School at Carlsruhe. Birnbaum was best known as an editor. He wrote several books upon analytical chemistry, and edited the "Handbuch der chemischen Technologie," after Bolley's death.

—On Feb. 27, A. P. Borodin, Professor of Chemistry in the Medical Academy at St. Petersburg.

CONTRIBUTIONS FROM THE LABORATORY OF
THE UNIVERSITY OF PENNSYLVANIA.

XXX

COMMUNICATED BY F. A. GENTH, JR.

SEVERAL of our students, having become sufficiently advanced in chemical manipulation to do trustworthy scientific work, were given various subjects for investigation. Of these the following gave results of more or less interest.

SEPARATION OF LEAD AND BISMUTH.

MR. HERMAN HERZOG, JR. made a series of experiments testing the principal methods for separating lead from bismuth.

1. Equal parts of both metals in solution as nitrates were treated with a slight excess of sulphuric acid and then heated until all nitric acid had been expelled, after which the solution was evaporated to complete dryness. Then dilute sulphuric acid (1.10) was added and, after digestion, the residue was filtered and washed with dilute sulphuric acid. A series of ten experiments showed that from 1.97 per cent. to 2.79 per cent. of the bismuth remained with the lead—the mean of the ten experiments being equal to 2.51 per cent.

2. A similar solution was evaporated in a like manner until fumes of sulphuric acid went off copiously and the mass had changed into a solid cake. It was then treated with acid as before. Ten experiments showed that from 1.05 to 1.31 per cent. of the bismuth (or a mean of 1.17 per cent.) remained with the lead.

3. Similar solutions were evaporated as before until fibrous crystals of bismuth sulphate appeared and fumes of sulphuric acid began to be evolved—then diluted with water and dilute sulphuric acid, etc. In ten experiments only 0.19 to 0.41 per cent. of the bismuth remained with the lead. (The mean was 0.28 per cent.) The latter method is the one generally made use of in the laboratory of the University—however, in order to recover the small amount of bismuth the lead sul-

phate is dissolved in hot sodium hydrate from which solution it is subsequently precipitated by sulphuric acid. The minute residue left behind is dissolved in dilute nitric acid, evaporated with an excess of sulphuric acid, filtered, washed, and the solution added to the main filtrate from the lead.

Nine series of five experiments each, which Mr. Herzog made, showed that the strength of the sulphuric acid used in washing was of great influence on the accuracy of the determinations. His results were :

<i>Strength of acid.</i>	<i>Bi₂O₃ left in the PbSO₄.</i>	<i>PbO found with Bi₂O₃.</i>
1:4	0.009	7.54
1:5	0.019	6.05
1:7	0.072	0.51
1:8	0.172	0.30
1:9	0.51	0.07
1:10	0.79	trace
1:15	1.11	"
1:25	2.91	"
water	3.21	0.13

Equal quantities of lead and bismuth were taken.

The addition of alcohol has proved to be of no advantage, and is recommended merely to remove the sulphuric acid from the lead sulphate precipitate after washing.

It was found that the addition of hydrochloric acid before precipitating the lead as sulphate is of no advantage; on the contrary, notwithstanding the greater solubility of the lead chloride, it is difficult to convert it into sulphate, the precipitate being often more chloride than sulphate even after standing for one day. Then also the bismuth, when precipitated in the filtrate by ammonium carbonate, contains oxychloride which on ignition will cause some of the metal to volatilize.

Experiments made to separate bismuth from lead as oxychloride gave from 2 to 5 per cent. of the lead with the bismuth; on redissolving and reprecipitating the bismuth contained only traces of lead.

The method of separating bismuth from lead as basic nitrate gave unsatisfactory results; *with bismuth alone* the average of ten analyses showed 99.89 per cent. of bismuth (maximum loss being 0.23 per cent., minimum, 0.09 per cent.).

If in presence of lead the evaporation is not carried far enough, bismuth will go in solution, whilst if carried so far as to render it insoluble from 8 to 11 per cent. of lead may be retained.

Liebig's method of precipitating bismuth by barium or calcium carbonate gave low results and was otherwise unsatisfactory.

In Ullgren's method of precipitating bismuth by metallic lead the excess of acid in the solution of the nitrates was removed by evaporation, after which the solution was supersaturated with acetic acid and a weighed strip of lead was kept immersed for twenty-four hours. The spongy bismuth was washed off, if necessary, removed with the aid of a feather, and collected in a weighed button of fusible alloy and weighed. The lead was determined either as a sulphate or chromate, and the amount lost by the lead strip deducted from the calculated amount. The following results were obtained:

AMOUNT IN GRAMS.

	1		2		3		4	
	<i>Taken.</i>	<i>Found.</i>	<i>Taken.</i>	<i>Found.</i>	<i>Taken.</i>	<i>Found.</i>	<i>Taken.</i>	<i>Found.</i>
Pb	0.5523	—0.5531	0.5619	—0.5621	0.6310	—0.6314	0.1020	—0.1018
Bi	0.2310	—0.2314	0.1921	—0.1922	0.0820	—0.0822	0.5200	—0.5208

Abel and Field's method of adding copper hydrate, or basic copper nitrate, to the solution which was nearly neutralized with ammonium hydrate, and then warming, gave good results although somewhat high in bismuth. In twenty determinations the maximum deviation was not over 0.20 per cent. above the amount of bismuth taken, and this can be reduced to a minimum by repeating the operation. The principal difficulty lies in the separation of the copper oxide from the bismuth oxide by ammonium hydrate which should be repeated; the lead may be separated from the copper by ammonium carbonate or by precipitating it from an *acetic acid* solution as chromate.

The volumetric methods tried were all found to be more or less complicated and liable to error. The well known chromate method gives very fair results. The method recommended by Haswell is to add sodium hydrate (or zinc oxide) to a nitric acid solution until a slight precipitate remains on standing; then to heat the solution to 60° C in a porcelain

vessel and to run potassium permanganate into it until the supernatant liquid remains pink after a few minutes standing. The results obtained were, on an average, about 0.7 per cent. too high. Of all the other volumetric methods none gave even approximate results.

A method which has not been mentioned in any works on analytical chemistry, or in such journals as we have access to, has been worked out by Mr. Herzog and possesses sufficient merit to be put on record. It is based on the fact that in a *neutral* solution of a bismuth salt, the bismuth is precipitated as a basic acetate on boiling with sodium acetate.

The following manner of working gave the best results: To the solution of the nitrates add sodium carbonate until a slight but distinct, permanent, flocculent precipitate is formed. Then shake or stir well which will change it to a pearly crystalline compound which settles rapidly. If now, on adding another drop of sodium carbonate solution to the clear liquid, a precipitate is formed, the solution is ready for the addition of sodium acetate, which should be done in the cold. Then the solution should be boiled vigorously for $1\frac{1}{2}$ to 2 hours, filtered while hot, and washed with boiling water. Redissolve in dilute warm nitric acid and precipitate the bismuth by ammonium carbonate. The lead in the filtrate may be precipitated as chromate, or carbonate. The seven series of analyses that were made, gave the following results:

No. of the series.	No. analyses in each series	Parts by weight taken.		Maximum per cent. found.		Minimum per cent. found.		Average per cent. of all analyses.	
		a	b	a	b	a	b	a	b
		Lead.	Bism'h	Lead.	Bismuth.	Lead.	Bismuth.	Lead.	Bismuth.
1	10	90	10	90.30	9.92	90.17	9.85	90.206	9.878
2	7	80	20	80.32	19.87	80.25	19.80	80.289	19.846
3	6	75	25	74.93	25.01	74.87	24.91	74.902	24.963
4	5	50	50	50.07	49.93	49.95	49.83	49.996	49.892
5	6	25	75	25.41	74.84	25.19	74.52	25.255	74.772
6	5	20	80	20.31	80.01	20.07	79.83	20.172	79.910
7	9	10	90	9.93	90.31	9.60	90.05	9.833	90.153

THE INFLUENCE OF MANGANOUS SULPHATE AND OTHER SALTS
ON THE TITRATION OF IRON IN HYDROCHLORIC ACID
SOLUTION BY POTASSIUM PERMANGANATE.

MR. DAVID L. LUKE has made a series of experiments, similar to those performed by the late Dr. Clemens Zimmerman, Kessler, Thomas, and others, studying the influence of

manganous sulphate and other salts on the titration of iron in hydrochloric acid solution with potassium permanganate. His results were mainly corroborative of what these investigators have already shown.

It was found that the presence of manganous sulphate in the hydrochloric acid solution of the ferrous salt would prevent, for a short while at least, the reduction of a greater amount of potassium permanganate than corresponds to the amount of ferrous salt in solution, and also that no free chlorine was detected on titration. Lead chloride acted in a manner similar to manganous sulphate.

Magnesium, cobalt, and copper sulphates were also tried but gave no good results, showing them to be of no value.

A very important precaution is to watch the end reaction in the hydrochloric acid solution containing MnSO_4 very closely, which can be distinguished by the first complete coloration throughout the liquid. If not stopped there, too much permanganate can be easily added because of the almost immediate fading out of the color of the first few cubic centimetres added after the end reaction was reached.

The solutions used were similar to those of Zimmermann. Hydrochloric acid = 1.12 sp. gr., H_2SO_4 = 1.84 sp. gr., a dilute solution of permanganate, with a titre of 0.0039603 Fe., and a stronger one of 0.0081136 Fe. Manganous sulphate solution 200 grams in 1 litre. Also a hot saturated solution of lead chloride.

(1) The first experiments were with ferrous ammonium sulphate and gave the following results:

No.	$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 + 6\text{H}_2\text{O}$	H_2SO_4	HCl	MnSO_4	$\text{K}_2\text{Mn}_2\text{O}_8$
1	0.7 gram.	15 c. c.			25.10 c. c.
2	0.7 "		10 c. c.		25.65 "
3	0.7 "		10 "	20 c. c.	25.10 "
4	0.7 "		20 "		25.75 "
5	0.7 "		20 "	20 "	25.10 "
6	0.7 "		40 "	20 "	25.20 "
7	0.7 "	15 "	20 "		25.50 "
8	0.7 "	15 "	20 "	20 "	25.20 "
9	0.7 "	15 "		20 "	25.20 "
10	0.7 "	15 "			25.20 "

The next experiments were made by fusing magnetite with potassium bisulphate, dissolving in water, reducing with zinc and titrating with the strong solution of permanganate.

No.	Iron Solution	HCl	MnSO ₄	K ₂ Mn ₂ O ₈
1	100 c. c.			37.75 c. c.
2	100 "	20 c. c.		38.00 "
3	100 "	20 "	20 c. c.	37.80 "
4	100 "	40 "		38.05 "
5	100 "	40 "	20 "	37.80 "

A similar hydrochloric acid solution of magnetite was made, reduced with zinc, and titrated with the same permanganate solution.

No.	Iron Solution	H ₂ SO ₄	MnSO ₄	K ₂ Mn ₂ O ₈
1	50 c. c.			38.00 c. c.
2	50 "	10 c. c.	20 c. c.	37.50 "
3	50 "	10 "	20 "	37.50 "
4	50 "	10 "	20 "	37.45 "

A ferro manganese dissolved in hydrochloric acid and titrated twice in presence and twice in absence of manganous sulphate gave each time the same result on titrating. It should be said that the ferromanganese contained about 65 per cent. manganese and 30.4 per cent. iron.

N. Wiley 'Thomas' method consists in substituting lead chloride for manganous sulphate and proceeding as before. A quantity of magnetite was therefore dissolved by Mr. Luke in hydrochloric acid, and titrations were made in presence of lead chloride, also manganous sulphate, and alone. The lead chloride was added as a hot, saturated solution.

No.	Iron Solution	PbCl ₂	MnSO ₄	K ₂ Mn ₂ O ₈
1	25 c. c.			16.00 c. c.
2	25 "	20 c. c.		15.60 "
3	25 "	30 "		15.60 "
4	25 "	20 "		15.60 "
5	25 "		20 c. c.	15.60 "
6	25 "		20 "	15.55 "

From the above results it will be observed that under the proper conditions, i. e., in presence of either manganous sulphate or lead chloride, Marguerite's method for the titration of iron will work in hydrochloric acid solution as well as in sulphuric acid.

ANALYSIS OF SPESSARTITE GARNETS.

MR. WM. C. ROBINSON, JR., made an examination of spessartite garnets found imbedded in a vein of orthoclase in granitic mica schist on the east side of the Schuylkill river, Fairmount Park, Philadelphia, Pa., and also under similar conditions at Avondale, Delaware Co., Pa.

The garnets were of a dark reddish brown color, varying in size up to 1 ½ or several inches in diameter. In thin sections, under the microscope no inclosures were observed—the sections were imperfectly transparent and of a dark hyacinth red color, the Avondale garnet being the darker of the two.

The Fairmount garnets are trapezohedral crystals 2 O 2. Hardness, 7. Sp. grav. 4.23. Numbers 1 and 2 represent analyses of the same.

	I	II
SiO ₂	38.273	38.214
FeO	13.580	13.621
MnO	25.390	25.207
CaO548	.523
Fe ₂ O ₃	2.260	2.280
Al ₂ O ₃	19.579	19.640
	<hr/>	<hr/>
	99.630	99.485

The Avondale garnet occurs as a combination of dodecahedron and trapezohedron, ∞ O, 2 O 2. Sp. grav. 4.12. The following analyses were made:

	I	II
SiO ₂	40.981	40.864
FeO	9.408	9.137
MnO	38.325	38.351
(Ca, Mg)O	tr.	
Fe ₂ O ₃	1.034	1.226
Al ₂ O ₃	9.269	9.575
	<hr/>	<hr/>
	99.017	99.153

Laboratory of the University of Pennsylvania, }
Philadelphia, Pa., April 11, 1887. }

THE METHODS OF MECHANICAL SOIL-ANALYSIS.*

BY THOMAS B. OSBORNE, PH. D.

THE following pages are a record of results so far obtained in investigating the processes that have been recently employed for separating soils mechanically into clay and various grades of sand and silt, with a view to the adoption of a method suitable for use in the study of Connecticut soils. It was at first proposed to make a comparison of three methods, viz: Schoene's, Hilgard's and Knop's as modified by Dr. G. E. Moore. While awaiting the construction of Hilgard's elutriator, and the arrival from Germany of Schoene's apparatus, the third above-named method was first examined. It is described by Dr. Moore, in his paper on "Tobacco Soils," in the final report of the 10th U. S. Census, vol. iii, pp. 872-3.

The Knop apparatus consists of a set of metal sieves with round holes of 3, 1, 0.5 and 0.25 millimeters diameter respectively, and a cylindrical glass jar of 36 millimeters caliber, carrying four lateral narrow tubes at intervals of 10 centimeters which may be opened or closed at pleasure by means of rubber tubes and clamps.

In Knop's process the soil is weighed out, boiled, and after removing with sieves all portions coarser than $\frac{1}{4}$ of a millimeter in diameter, is placed in the cylinder and water added till its level is 10 centimeters above the upper side tube. The cylinder is then closed with a rubber stopper, shaken violently, set up as nearly vertical as possible and the soil allowed to settle for 5 minutes. The upper side tube is then opened and the water and fine sediment drawn off. At intervals of 5 minutes the other side tubes are opened successively. The cylinder is then refilled, and these operations are repeated. The process is continued until no turbidity is seen in the water drawn off. The sediment remaining in the cylinder is called by Knop "fine sand," that deposited from the washings "dust."

*From Report of the Connecticut Agricultural Experiment Station for 1887. Communicated by the author.

Dr. Moore, in the Census Report, calls attention to the fact that the "finesand" thus obtained by following Knop's method can be of no definite grade, for the reason that as the particles settle they continually collide and interfere with one another and hence do not subside with velocities strictly depending on their dimensions. The effect of these collisions will vary with the number and size of particles in the liquid, and since both their number and size constantly change as the subsidence is prolonged, the size of the particles collecting in the bottom of the cylinder will necessarily be far from uniform. Dr. Moore obviated this difficulty by repeatedly working over his sediments in Knop's cylinder as long as any further separation took place, and, on microscopic examination of the final sediments, he found that a *very* sharp separation had been obtained. These operations, while effective, are so exceedingly tedious as, in our view, to make the method impracticable for extended use.

On attempting to operate Dr. Moore's process, it shortly became evident that nothing is to be gained by limiting sedimentation arbitrarily to any particular intervals of time or space, and it appeared probable that all desired separations could be most simply and easily effected by systematically repeated decantations from beaker glasses with frequent use of the micrometer to control the results.

Attention was therefore turned to this mode of working, and experience thus far indicates that the simple method, which we may designate "Beaker elutriation," is not inferior to any yet proposed as respects accuracy and convenience.

The principles on which this method rests may be gathered from the following considerations:

When a soil is completely suspended in water by vigorous agitation, particles of all the sizes present are to be found throughout the entire mass of liquid. When subsidence takes place, the larger particles will go down more rapidly than the smaller ones, but some of the small particles that are near the bottom will be deposited sooner than some of the larger ones which have a much greater distance to travel. Thus, independently of the fact that the large particles in their descent are somewhat impeded by the smaller—the smaller being at

the same time somewhat hastened by the larger—the sediment that reaches the bottom at any moment is a more or less complex mixture of all the mechanical elements of the soil. The liquid, however, above this sediment at the same moment will have completely deposited all particles exceeding certain dimensions, or hydraulic value, determined mainly by the time of subsidence.

If now the aforesaid first sediment be suspended in pure water, and allowed to subside for the same time as before, the larger part of it will be again deposited, but some will remain in suspension, consisting of a considerable part of the finer matter of the first sediment. By pouring off these suspended particles with the water and agitating the sediment again with clear water as before, another portion of fine particles will be suspended and may be decanted from it. On continuing this process of repeated decantations it will soon be found that the soil has been separated into two grades.

It is evident that in this way a separation can be made, but it is perhaps not so clear that such a separation would be sharp enough for the purposes of a mechanical soil-analysis. If for instance the separation is to be made at .05 millimeters diameter, it is evident that by repeated decantations all below .01 millimeter can be washed out of that above .05 millimeters, but it may not appear so probable that all below .045 millimeters can be removed without removing some above .055 millimeters.

Such a result may be easily attained, however, if the following principle is adhered to:

Make the duration of the subsidences such that the *liquid* decanted the first few times shall contain nothing *larger* than the desired diameter. Then decant into another vessel, timing the subsidence so that the *sediment* shall contain nothing *smaller* than the chosen diameter. This can not be done without decanting much that is larger than the chosen diameter, but the greater part of the particles greater and less than the chosen diameter can be removed and an intermediate product obtained, the diameters of whose particles are not very far from that desired.

The reason for first removing the greater part of the coarse particles lies in the fact that as they rapidly subside they drag down with them much of the fine material, and render it difficult to effect a sharp separation in their presence. If then we bear in mind the general principle that repeated subsidences and decantations properly timed will gradually remove the fine particles from the coarse, and also the fact that the removal of the particles much above and much below the limits of any desired grade, greatly facilitates the separation of that grade, there will be no difficulty in obtaining satisfactory results after a little practice. In developing this method, we proceeded as follows:

The Sample.—Unless care is used in selecting the portion to be analyzed considerable discrepancies are liable to be found between duplicate analyses. We usually prepare several pounds of air-dry “fine earth” by passing the soil through a sieve of 3 millimeters mesh to remove the gravel, etc., mix as thoroughly and uniformly as possible, and weigh off for analysis thirty grams taken in many small portions from different parts of this sample.

Sifting.—The weighed soil is at first stirred up with 300 or 400 cc. of water and then thrown successively upon sieves with circular holes of .1, .5, and .25 mm. diameter respectively. Affusions of water and a camel's hair brush are used to cause all the fine material to pass through the sieves which, towards the last, are agitated under water in a shallow dish so that the soil is immersed. The finest sieve should be well wet with water on its lower surface just before use. The finest particles which render the water turbid are easily washed through. The turbid water is kept separate from the clear water which comes off with the last portions that pass the sieves. The turbid water usually does not amount to more than one liter.

Elutriation.—The separations made by elutriation have as yet been mostly confined to three grades, the diameters of which are from .25 to .05^{mm}; .05 to .01^{mm}; and .01 to 0^{mm}. For present convenience of description, we will call those particles having diameters between .25 and .05^{mm}, sand; those between .05 and .01^{mm}, silt; and those below .01^{mm}, dust (or dust and clay).

After the turbid liquid from the siftings has stood a short time it is decanted from the sediment, and on further standing long enough to form a slight deposit, is again decanted and this slight sediment is examined carefully with the microscope, when if the first subsidence has been long enough, it is found to consist wholly of "silt" and "dust" and is free from "sand." If "sand" be present, the subsidence of the turbid liquid is continued until no more "sand" is to be seen in the sediment. As the "sand" subsides rapidly there is no difficulty in freeing the liquid first decanted, altogether from this grade of particles. The sediment obtained in this way contains all the "sand" and also some "dust" and much "silt." As only "dust" and the finest "silt" render the water turbid, the sediment is stirred up a few times with fresh quantities of water and decanted after standing long enough to let *all* the "sand" settle. When the water decanted is free from turbidity, the last portions of the soil passing through the sieve with the clear water are added to the sediment and the decantations continued so as to remove most of the "silt." When no more "silt" can be easily removed from the sediment without decanting "sand," the decantations are made into a different vessel and the subsidences so timed as to remove as much as possible of the "silt." By using a little care at least three-quarters of the "sand" is thus obtained free from "silt." The rest of the "sand" is mixed with the greater part of the "silt" which has been decanted into the second vessel. The size of the smallest particles in this vessel is determined with the microscope, to make sure that its contents are free from "dust" as they usually will be if, after settling for a few moments, they leave the water free from turbidity.

We have thus separated the soil into three portions, one containing sand, one sand and silt, and the other silt, dust and clay. The sand and silt are separated from each other by repeating the subsidences and decantations in the manner just described.

In this way there is removed from the sediment, on the one hand, a portion of silt free from sand and dust, and on the other hand a portion of sand free from silt. Thus is obtained

a second intermediate portion consisting of sand and silt, but less in amount than first and containing particles of diameters much more nearly approaching $.05^{\text{mm}}$. By repeating this process a few times, this intermediate portion will be reduced to particles whose diameters are very near $.05^{\text{mm}}$ and which may be divided between sand and silt, according to judgment. In our work the amount of this has always been very small. As soon as portions are separated, which the microscope shows to be pure sand or pure silt, they are added to the chief portions of these grades already obtained.

The same process is applied to the separation of silt from dust. When all the silt has been removed from the dust and clay, the turbid water containing the dust and clay is set aside and allowed to settle in a cylindrical vessel for 24 hours. The vessel is filled to a height of 200^{mm} . According to Professor Hilgard, whose directions we have followed substantially in most cases, the separation of the dust from clay during a subsidence of 24 hours, will give results of sufficient accuracy, although the clay then remaining suspended will not be entirely free from measurable fine particles up to $.001$ or $.002^{\text{mm}}$ diameter.

Small beakers and small quantities of distilled water are used at first for the decantations, as thus the duration of subsidence is less and more decantations can be made in a given time than when larger quantities of water are employed. Beakers of about 100^{cc} capacity are convenient for the coarser grades, but it is necessary to use larger vessels for the fine sediments from which turbid water accumulates that cannot be thrown away, as may be done with the clear water, from which the coarse sediments settle out completely in a short time.

It is best to keep the amount of water as small as possible in working out the dust since loss is incurred in using too large quantities.

Measurement of the Particles.—The measurement of the particles requires a little practice on account of the confusion occasioned by the organic matters and mica. One soon learns, however, to distinguish between these and the *quartz grains* whose average diameter is properly taken as the standard.

In order to determine the size of *particles in suspension* we have found it convenient to apply to the surface of the liquid a small glass tube, in such a way as to take up a single drop, which is transferred to the glass slide. This drop will contain the smallest particles in the liquid. To obtain a sample of the coarsest particles the liquid is allowed to stand long enough to form a very slight sediment, and a portion of this sediment is collected with the glass tube. To determine the diameter of the *particles in a sediment*, it is stirred up vigorously with a little water and the pipette at once applied to the surface of the water. The drop thus taken contains the small particles. On decanting off the greater part of the sediment, the large particles remain at the bottom of the beaker and may be easily examined.

Time.—The time required to make the separations above described, is about two hours for each, so that an analysis including the siftings, is made in five or six hours, exclusive of the time necessary for collecting the dust and separating the clay, for which a subsidence of twenty-four hours has been allowed.

Weighing.—The sediments have been prepared for weighing by allowing them to subside completely, decanting off the clear water as far as possible, rinsing them into a weighed platinum dish, and igniting. Care must be taken in cooling the ignited sediments as they are exceedingly hygroscopic.

Beaker-Elutriation of Sandy Soils.—The working of this method is illustrated by the subjoined results of repeated analyses obtained on sandy drift-soil from the garden of the Experiment Station. These are the first analyses made while acquiring experience of the method. In order that the several elutriations may be strictly compared and that the variations arising from the sifting process and clay-separation may be eliminated, the results given below have been calculated in the following manner: The average amount removed by the sieves was carefully determined in several trials, and the difference between this average and the amount removed by the sieves in each analysis was noted. When more than the average amount remained on the sieve, the noted difference was added to the coarsest grade separated by elutriation, when less re-

mained on the sieve, the difference was subtracted from this grade. It rarely happened that less remained, and then only a few hundredths of a per cent., for the chief source of error in sifting arises from the difficulty with which the last portions pass through the sieve. These last portions consist of particles having diameters nearly the same as, or in some directions even greater than the holes of the sieve, and hence the differences due to their imperfect removal properly fall on the coarsest grade subjected to elutriation. All errors due to incomplete separation of the clay fall on the finest grade, and therefore this grade, together with the clay, is here calculated by difference.

SURFACE SOIL, GARDEN OF EXPERIMENT STATION, NOT BOILED.
Two Elutriation-products.

	No. 5.	No. 8.	No. 13.	No. 14.	No. 15.
Removed by sieves	48.82	48.82	48.82	48.82	48.82
.25 .01 ^{mm}	36.84	36.35	35.70	36.53	35.98
.01 0 ^{mm} (by difference) . . .	7.51	8.00	8.65	7.82	8.37
Loss on ignition of the soil . . .	6.83	6.83	6.83	6.83	6.83
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The maximum differences above amount to 1.1 per cent. of the soil. In the subjoined analyses we have three elutriation-products on unboiled soil with greatest difference of 2.2 per cent.

	No. 13.	No. 14.	No. 15.
Removed by sieves	48.82	48.82	48.82
.25 .05	21.06	23.28	22.77
.05 .01	14.64	13.25	13.21
.01 0 (by difference)	8.65	7.82	8.37
Loss on ignition of the soil	6.83	6.83	6.83
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The Effect of Boiling.—As it is now generally considered indispensable to boil a soil for some time before subjecting it to mechanical analysis, a number of analyses were made after boiling the samples for 23 hours with water substantially as recommended by Hilgard. The results obtained are as follows :

SURFACE SOIL, GARDEN OF EXPERIMENT STATION. Boiled for 23 hours. Two elutriation-products. Greatest difference 2.2 per cent. of soil.

	No. 6.	No. 7.	No. 9.	No. 16.	No. 17.	No. 18.
Removed by the sieves . . .	47.77	47.77	47.77	47.77	47.77	47.77
.25 .01	33.34	32.85	32.84	31.47	32.25	31.15
.01 o (by difference) . .	12.06	12.55	12.56	13.93	13.15	14.25
Loss on ignition of the soil .	6.83	6.83	6.83	6.83	6.83	6.83
	100.00	100.00	100.00	100.00	100.00	100.00

Three elutriation-products. Greatest difference 2.3 per cent.

	No. 9.	No. 16.	No. 17.	No. 18.
Removed by the sieves	47.77	47.77	47.77	47.77
.25 .05	20.40	21.34	20.59	20.66
.05 .01	12.44	10.13	11.66	10.49
.01 o (by difference)	12.56	13.93	13.15	14.25
Loss on ignition of the soil	6.83	6.83	6.83	6.83
	100.00	100.00	100.00	100.00

In the foregoing analyses "clay" has not been considered independently of "dust," in the product of .01 to 0^{mm} diameter.

Comparison of results on soil boiled, soil not boiled and soil simply pestled.—The effect of boiling on the surface soil of the Experiment Station garden is most clearly seen from the sub-joined comparison of the averages of the foregoing more de-tailed analyses of that soil.

No. 29 is an analysis made on a sample of this soil not boiled in which the sediments were, at the last, worked under a soft rubber pestle by gentle pressing down (but not grinding around), so long as such treatment appeared to detach any fine particles.

The figures for clay in the following statement are reckoned by difference or loss after the other ingredients had been ob-tained by direct weighings.

SURFACE SOIL FROM EXPERIMENT STATION GARDEN

	Av. of 4 analyses. Boiled.	No. 29. Pestled.	Av. of 3 analyses. Not Boiled.
Removed by sieves	47.77	48.82	48.82
.25 .05	20.75	22.44	22.37
.05 .01	11.18	12.55	13.70
.01 o	10.72	7.36	7.20
Clay (by difference)	2.75	2.00	1.08
Loss on ignition	6.83	6.83	6.83
	100.00	100.00	100.09

The effect of boiling sandy soils is further illustrated in the following instances:

SUB-SOIL FROM EXPERIMENT STATION GARDEN.

	No. 19. Not Boiled.	No. 20. Boiled.	No. 21. Boiled.
Removed by sieves	41.60	39.33	39.33
.25 .05	35.93	32.35	32.95
.05 .01	12.13	10.32	10.37
.01 0 (by difference)	5.24	8.29	7.64
Clay (direct)	1.02	5.63	5.63
Loss on ignition	4.08	4.08	4.08
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

SANDY LOAM FROM DURHAM, CONN.

	No. 12. Not boiled.	No. 10. Boiled 23 hours.
Removed by sieves	16.19	14.07
.25-.05	29.52	25.10
.05-.01	23.17	23.12
.01- 0	9.65	15.42
Clay (by difference)	1.67	2.49
Loss on ignition	19.80	19.80
	<hr/> 100.00	<hr/> 100.00

The analyses of these sandy soils show a very decided increase in the quantity of particles smaller than .01 mm. diameter at the expense of those coarser, as a result of boiling. The surfaces of the coarser particles which have been boiled are seen to be polished and of a lighter color than those not boiled. The surfaces of the unboiled grains are coated with a film of fine material cemented to them probably by clay. When these coarse particles which have not been boiled are violently stirred with water for a short time no fine particles are detached from them, and a careful examination under the microscope fails to reveal in any of the sediments more than an occasional grain exceeding the .05 mm. limit by so much as .01 mm., or the .01 limit by .005 mm. It would therefore appear that these small particles thus set free by long boiling are really a part of the larger ones, and should be treated as such in a mechanical analysis of these soils.

In case of the pestled soil No. 29, there is a gain on clay and a loss on the .05-.01 mm. sediment of about one per cent. as

compared with the unboiled soil, but as the intermediate grade is quite the same in both, the difference is not due so much to scouring of the sediments as to their unlike separation. In fact, the pestling was seen to release very little fine matter from the sediment as first elutriated.

In the analyses that follow the soils were simply pestled.

No. 36, Sandy Loam, Drift Soil, Deer River, New York. A fairly good soil when treated with stable manure.

No. 38, "Blowing Sand," Alluvial Soil, valley of Connecticut River, East Windsor, Conn. Twenty-five years ago considerable tracts of this soil, which had been "skinned" by constant cropping with rye until the yield was reduced to 8 to 10 bushels per acre once in two or three years, were lying waste and in exposed situations drifted with the winds, but having bottom-water at the depth of a few feet were readily reclaimed by means of clover-seed and sheep.

No. 39, "Clay Soil," East Windsor. An alluvial silt so fine as to pass for clay.

			Sandy Loam. No. 36.	Blowing Sand. No. 38.	"Clay Soil." No. 39.
2.	mm-1.	mm	1.57	1.18	. . .
1.	-.5	3.15	3.44	. . .
.5	-.25	27.30	12.86	1.22
.25	-.05	40.77	68.62	6.81
.05	-.01	8.38	4.46	69.11
.01	-0	8.07	6.30	17.83
Clay	2.00*	0.25*	2.97*
Loss on ignition	7.66	3.06	2.60
			98.90	99.92	100.54
			*Direct.		

Comparison of Beaker Elutriation with Hilgard's Churn Elutriation.

The churn elutriator employed, while differing somewhat in the details of its construction from that originally described by Prof. Hilgard, (Am. Jour. Sci., Oct. and Nov. 1873), closely follows that description in all essential points, and has very nearly the same interior dimensions. The body of the instrument was cast from nickel bronze so as to resist the wear of sediments. The axle bearing the grated wings passes through

a stuffing box packed with greased cotton like those employed in steam engines. The other end is covered by a cap which screws water-tight over the end of the axle. By these means leakage is entirely prevented. Just above the axle the spherical body is divided horizontally into two parts which fit together accurately, the upper part screwing into the lower. This gives opportunity of cleaning the instrument. The interior is carefully turned to a hollow sphere of the dimensions indicated by Hilgard. The glass cylinder is fastened by a collar which screws into the body. The grated wings were cast from nickel bronze and patterned from a drawing kindly furnished by Prof. Hilgard. The instrument has two strong legs with broad feet, cast as part of the body, and the latter were carefully planed so that the instrument stands vertically when secured upon a level table. A glass reservoir is attached as described by Hilgard, and this communicates with a constant-level water tank. The rate of water supply is regulated by a cock, as Hilgard recommends. Motion is communicated to the grated wings by means of a pulley at the end of the axle which is belt-gearred to a water motor. The instrument thus constructed* has proved entirely satisfactory, having been in operation many weeks without serious leak or wear.

Results on Sandy Soils.—The following tables give analyses of coarse soils by the two methods of beaker and churn elutriation, the samples being alike prepared by boiling for 23 hours :

SOIL FROM EXPERIMENT STATION GARDEN.

Surface soil—boiled 23 hours.

	Churn Elutriation. VII.	VIII.	Beaker Elutriation. Average of four analyses.
Removed by sieves . .	47.77	47.77	47.77
.25-.05	22.06	21.95	20.75
.05-.01	11.20	11.62	11.18
.01-0	9.82	9.14	10.72
Clay (difference) . . .	2.32	2.69	2.75
Loss on ignition . . .	6.83	6.83	6.83
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

*By Mr. J. M. Beers, machinist, New Haven.

Subsoil—boiled 23 hours.

	Churn Elutriation.		Beaker Elutriation.	
	X.	XI.	20.	21.
Removed by sieve	39.33	39.33	39.33	39.33
.25-.05	33.61	30.83	32.35	32.95
.05-.01	10.91	12.25	10.32	10.37
.01-0	7.05	8.11	8.29†	7.64†
Clay	5.02†	5.40†	5.63	5.63
Loss on ignition	4.08	4.08	4.08	4.08
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

These analyses agree quite as well as could be expected for two such different methods.

According to Hilgard the results of duplicate churn elutriations usually agree within 5 per cent. of the amount of the sediment. Greater practice in working the churn elutriator will doubtless enable us to obtain more concordant percentages than those here given, which are first attempts.

The comparison we think sufficiently demonstrates that the method by beaker elutriation may properly assume equal rank, in respect to accuracy of separation, with that of Hilgard.

Several attempts were made to use the churn elutriator on these coarse soils without previously boiling, but, like Hilgard, we did not succeed in obtaining uniform results—evidently because the rapid and long continued churning of the soil has the same scouring effect on the sand grains that has been shown to be a result of protracted boiling, and there is consequently a continual abrasion and delivery of fine material throughout the entire elutriating process.

It is difficult to remove all the fine material even on a boiled sample of soil with the churn elutriator, but after some hours the amount passing off with the water is so trifling that the error due to this cause may be neglected. Microscopic examination of the sediments shows a very good separation indeed.

It is important to have water very free from any suspended matter in order to maintain a uniform current. It was found necessary to use distilled water for the low velocities, as the pipe water of the laboratory, although apparently clear, soon clogged the stop-cock.

†By difference.

Elutriation of Clayey Soils.—In applying beaker elutriation to tenacious fine-textured soils the matter of preliminary treatment had to be considered from the outset since Hilgard found that his churn elutriator gave no concordant or satisfactory results on clays without long boiling and subsequent “kneading” of the finer sediments. The first clay-soil examined is the one occurring at North Haven, Conn., which is extensively used in brick manufacture. The air-dry soil analyzed is reddish-brown in color, the lumps have but moderate coherence, being mostly crushed with ease between the fingers. It effervesces moderately with acids, and is fusible at high temperatures. A sample of this soil was boiled 23 hours and subjected to sifting and to beaker elutriation. On examining the sediments microscopically it was found that they contained many aggregations of extremely small particles which broke into “dust” under the pressure of the thin glass slide-cover. The sediments were then gently crushed or pestled in the beakers with help of a soft perforated rubber stopper (with a glass rod for handle), grinding together of the particles being as much as possible avoided. This pestling was continued with addition of clear water as long as it occasioned turbidity.

Other samples of the unboiled soil were subjected to the same treatment. Comparison of the analyses which follow shows that practically identical results are thus obtained *on this particular soil*, whether it be boiled or not, and indicates that the sediments are reduced to their elements by gentle pestling alone.

As above stated, simple boiling for 23 hours failed to break up the clay of this soil to any adequate extent.

The subjoined percentages were obtained in elutriation of different portions of the North Haven clay. The loss on ignition was ascertained in a special trial. In No. 27 all the determinations except loss on ignition, were made directly on one sample. In XII clay is reckoned by difference.

BRICK CLAY, NORTH HAVEN, CONN.

	Not Boiled.				Boiled 23 hours.	
	Beaker Elutriation				Churn Elutriation.	
	Thoroughly Pestled				Slightly Pestled.	Not Pestled.
	No. 24.	No. 25.	No. 27.	No. 28.	No. 26.	XII.
Removed by sifting,	3.41	3.27	3.49	3.49	3.41	3.36
.25-.05 ^{mm}	1.61	1.50	1.29	1.42	1.41	1.21
.05-.01	26.24	27.21	27.02	26.36	30.46	28.27
.01-0			52.21			56.29
Clay			10.15			4.92
Loss by ignition .			5.95			5.95
			100.11			100.00

We notice that the figures for the first two grades agree substantially throughout. The sediments .05-.01^{mm} in all the thoroughly pestled samples, boiled or unboiled, accord to within 1 per cent. The churn-elutriated sediment is 1½ per cent. higher, the slightly pestled sediment is 4.7 per cent. higher than the average of the thoroughly pestled sediments of the same grade.

In No. 27 the two grades .01-0^{mm} and clay were carefully worked over until their separation was carried to the furthest practicable limit or until the clay contained but a trifling proportion of measurable particles. Professor Hilgard insists that in some soils at least 30 hours lively boiling and repeated *kneading* of the finer sediments is indispensable for their reasonably complete separation. The comparison between No. 27 and XII is therefore not one of beaker vs. churn-elutriation, so much as one of pestling vs. 23 hours boiling and subsequent churning.*

*I have not attempted to employ kneading or pestling in connection with churn-elutriation. It is evident that the pestling of 15 to 30 grams of soil at once, *preliminary* to elutriation, is objectionable, because the operator has no ready criterion for deciding, either when the process has gone far enough to break up aggregated particles of soil, or when it has reached the point of pulverizing fragments of soft rock. To knead and work over in the churn elutriator, the sediments that have once passed it, would be effectual but very tedious. In beaker elutriation pestling is much more easily applied to finish the sediments that have been already obtained approximately pure, and the turbidity produced in the small portions of clear water used, indicates the effect of the pestling and shows how far to carry it.

With exception of the clay, the sediments consist essentially of water-worn quartz grains, in all respects except size, similar to those of the soil from the Experiment Station garden. The clay is in fact an alluvial deposit in the former bed of the Quinnipiac river, derived from the same drift which constitutes the soil of the Experiment Station garden.

In case of No. 27, the sediments .05-.01 and .01-0 were each further divided into two grades. The more detailed analysis is as follows:—

BRICK CLAY, NORTH HAVEN, CONN.		Detailed analysis. Thoroughly pestled.
Removed by sifting		3.49
.25-.05		1.29
.05-.02		7.21
.02-.01		19.81
.01-.005		22.02
.005-.0		30.19
Clay		10.15
Loss on ignition		5.95
		100.11

The soil next examined was a clay loam from Deer River, N. Y., of very different characters, containing a considerable proportion of water-worn fragments of soft and superficially disintegrated slaty rocks. On this account it serves well for studying the processes that may be used in the treatment preparatory to mechanical analysis.

CLAY LOAM, DEER RIVER, LEWIS CO., NEW YORK.*					
Beaker Elutriation.				Churn Elu'n.	
	Not boiled but thor- oughly pestled.	30 grms. boiled 23 hours with 350 c. c. water in ¼ liter flask.	30 grms. boiled 23 hours with 350 c. c. water in ¼ liter flask.	23 hours with 600 c. c. water in 1 liter flask.	15 grms. boil'd 23 hours with 600 c. c. water in 1 liter flask.
	No. 30.	No. 31.	No. 32.	No. 34.	XIII.
Removed by sifting	20.92	19.91	14.69	13.89	17.94
.25-.05	17.96	18.41	18.12	18.83	19.32
.05-.01	25.26	26.94	21.42	19.40	24.66
.01-0	23.05	22.00	28.14	33.13	24.25
Clay	3.55	4.75†	9.39	6.76†	5.84†
Loss on ignition	7.99	7.99	7.99	7.99	7.99
	98.73	100.00	99.75	100.00	100.00

*Note by the Director.—This very superior soil was selected for mechanical analysis because the Director was formerly for years quite familiar with its

The above analyses plainly demonstrate that for this soil pestling is a much safer treatment than boiling. Pestling gives 20.42 per cent. of material larger than .25^{mm} as the average of two determinations that differ 1 per cent. Boiling for 23 hours abrades these fragments of shale and slate to the extent of 2.5 per cent. when 15 grams of the soil are boiled in 600 c. c. of water, while, when 30 grams are boiled in but 350 c. c. of water, the scouring amounts in two trials, to 5.7 and 6.5 per cent. respectively.

The first sediment, .25-.05^{mm}, is remarkably alike in amount in all the elutriations, the extremes differing but by 1.4 per cent. This fact indicates that in boiling it yielded as much to the finer grades as it gained from those coarser, or else that it consisted of quartz sand which suffered no considerable change. It does in fact largely consist of colorless transparent quartz grains, but these are intermixed with others of a brown color, some translucent on the edges and others quite opaque, and all the sediments except "clay" are quite alike in appearance under the microscope, both from the unboiled and boiled soils. To the unassisted eye the boiled sediments seen in mass, are whiter or lighter in color than those unboiled, evidently the result of scouring of the sand grains. In the part removed by sifting many fragments of slate or shale are to be

qualities under tillage and cropping as well as with the geological elements from which it is formed. When the sample was taken, some 25 years ago, this land was and for more than 30 years had been capable of yielding 30 to 40 bushels of wheat per acre without manure. It had excellent texture, admitted of easy tillage when not too moist, was naturally well drained by the admixed and underlying gravel, and yet was retentive of moisture and suffered little under drouth. It retains to this day a high repute. The soil lies at the confluence of the Deer River with Black River and is an alluvium formed partly from the granitic drift that covers the adjacent higher land and partly from the disintegration of the soft rocks of the Lower Silurian that overlie each other in a long stretch of terraces and hills to the westward. Through these rocks Deer River and other tributaries of Black River have cut deep channels, and the soil contains a considerable proportion of water-worn gravel stones up to 2 inches or more in diameter, but commonly less than ½ inch in thickness, with well-rounded edges, derived from the Trenton Limestone, the Utica Slate, and the Lorraine Shales of the New York geologists. The soil as analyzed had been freed by sifting from material coarser than 2^{mm} diameter and contained 5.4 p. c. from 2 to 1^{mm}, 6.3 p. c. from .1 to .5^{mm}, and 9.2 p. c. from .5 to .25^{mm}.

†Clay and loss, by difference. All other determinations are direct.

seen, but none are detectable in the finer grades. It would appear therefore that when the weathered slate and shale get reduced to near 1^{mm} in thickness they lose all coherence and fall to sand, dust or clay. The brown, partly transparent, partly opaque particles, are probably bits of fine-grained argillaceous sand rock from the Lorraine Shales. The fragments of this rock apparently break up by the attrition of boiling, into the sand-grains of various dimensions from which the rock was originally formed.

In the $.05-.01^{\text{mm}}$ sediment the scouring effect of ebullition is again manifest and is evidently greater, as the friction of the grains of soil upon each other is increased by diminishing the volume of water with which they are boiled.

The matter detached by boiling from the foregoing grade is found in the two following, which in the extreme cases are 5.6 and 10.6 per cent. above the corresponding ones obtained from the unboiled but pestled earth.

The "clay" in analyses 30 and 32 as given above, was separated from silt ($.01-0^{\text{mm}}$) by 24 hours settling of the latter.

The following analysis was made on the fine earth of a fertile soil, from South Onondaga, New York, which originally contained a considerable proportion of slaty gravel and was derived in part from the limestones, slates and shales of the Upper Silurian and Lower Devonian. It is seen to be very similar in structure as it is in geological character to the clay loam from Deer River.

WHEAT SOIL, SOUTH ONONDAGA, NEW YORK.

	Beaker elutriation. Thoroughly pestled. No. 37.
Above 1^{mm}	6.96
.1-.5	5.45
.5-.25	5.17
.25-.05	9.07
.05-.01	26.35
01-0	29.43
Clay, by difference	8.10
Loss on ignition	9.47
	<hr/> 100.00

The last analyses to be mentioned in this paper have been made on an extremely fertile Prairie Soil.

PRAIRIE SOIL FROM MERCER CO., ILL.

	Thoroughly pestled.		Boiled 23 hours.
	No. 33.	No. 34.	XIV.
Siftings62	.92	.57
.25-.05	2.42	2.89	5.69
.05-.01	43.58	42.86	46.95
.01-0	31.58	31.44	26.74
Clay	5.81	7.40*	5.56*
Loss on ignition . . .	14.49	14.49	14.49
	<hr/> 98.50	<hr/> 100.00	<hr/> 100.00

*Clay and loss, by difference.

Here again, in a soil consisting almost entirely of matter finer than .05 mm., long boiling and churning are quite insufficient to prepare properly for elutriation. The cementing material in this prairie soil is evidently, to a large extent organic matter. The churn-elutriated sediments were all black. The first two sediments in the other analyses were nearly white after pestling, the organic matter in company with the finest mineral substance being thus transferred to the last two grades.

The trials made thus far appear to justify the following conclusions:

1. On sands and silts of pure quartz or similar resistant material Hilgard's method and Beaker elutriation give practically identical results.

2. With coarse sands and silts upon whose grains finer matter has been cemented by silicates, etc., and with soils containing soft slaty detritus, the churn elutriator with preliminary boiling may give results too low for the coarse and too high for the finer grades. In these cases beaker elutriation with pestling yields more correct figures.

3. Some loamy soils containing no large amount of clay or of extremely fine silt, as well as prairie soils rich in humus, cannot be suitably disintegrated by 24 hours' boiling, but are readily reduced by pestling.

4. Beaker elutriation preceded by sifting, gives results in 5 or 6 hours with use of 2 to 3 gallons of pure water, which in

churn elutriation require several days and consume 7 to 10 gallons of pure water.

5. Hilgard "found that practically 0.25^{mm} is about the lowest velocity" (of water-current per second) "available within reasonable limits of time" in his elutriator. Such a current carries over particles up to $.015^{\text{mm}}$ diameter and hence the silts of less dimensions cannot be conveniently separated by churn elutriation. In beaker elutriation there is no difficulty in making good separations at $.01^{\text{mm}}$ and at $.005^{\text{mm}}$.

6. Beaker elutriation requires no tedious boiling or preliminary treatment and with careful pestling of the sediments gives, we believe, as nearly as possible, a good separation of adhering particles and at every stage of the process carries with it, in the constant use of the microscope, the means of testing the accuracy of its work and of observing every visible peculiarity of the soil. It is not claimed that pestling may not easily go too far, but in any case a good judgment may be formed of its effects and of the extent to which it is desirable to carry it.

7. In beaker elutriation the flocculation of particles occasions little inconvenience and does not impair the accuracy of the results.

Further investigations are required on the fine matter of stiff clays and of soils rich in humus. Such it is contemplated to undertake immediately.

Before concluding this paper I must acknowledge my constant indebtedness to Prof. Hilgard and to Dr. Moore for the assistance derived from their publications and for the descriptions, sketches and apparatus supplied by them to this Station, which have been available for my work.

Time has not as yet permitted any extended study of Schöne's method as practiced by Orth, Fesca and Wahnschaff, and we can only say, from a few trials in its use, that it is certainly open to very serious objections, as Hilgard has pointed out.

NOTES ON ANALYTICAL METHODS.*

BY DR. T. B. OSBORNE.

FILTRATION OF CRUDE FIBER.

THE filtrations in the process of determining crude fiber are commonly quite difficult and tedious, the acid liquids especially, either running turbid through a coarse filter or clogging a fine one. In most cases these troubles may be avoided by using the filter-pump and a paper filter supported on a platinum cone and by breaking the filter down the fold or crease, on one side. This is done by folding the paper so as to form a cone of an angle slightly less acute than the funnel, placing it in the latter, moistening and then applying the suction when the paper will usually tear apart, leaving a narrow rift from the vertex upward, across which stretches a loose network of fibers. If the sample has not been too finely ground it may be filtered clear by shaking or stirring up thoroughly and throwing quickly on to the paper so that the coarser particles will hold the finer and prevent the latter from passing the rift or clogging the paper. The break allows the solution to run off rapidly so that in most cases but three or four minutes are necessary to conclude the filtration.

This method has given good results in crude fiber determinations with hay and bran-feed and with sheep-dung, which were very difficult to manage by the usual methods.

FILTRATION AND WEIGHING OF SILVER CHLORIDE.

Solutions containing organic matter are often very difficult to filter from silver chloride, this precipitate at first running through and afterwards clogging the paper so as to make the filtration slow. The removal of the precipitate from the paper and the conversion of the reduced silver obtained after burning

*From Report of the Connecticut Agricultural Experiment Station for 1887. Communicated by the author.

into chloride again, are operations taking considerable care and time. In many cases it is better to allow the precipitate to settle and to decant the greater part of the liquid through a Gooch asbestos filter. The precipitate is then dissolved in a very slight excess of ammonia water, the concentrated solution being thereupon made slightly acid with nitric acid, the precipitate will separate in a flocky form, which after carefully washing by decantation may be thrown on to the filter and sucked dry with the pump without danger of running through. If the precipitate be fused it is somewhat difficult to remove from the crucible, but it may be dried at 100° , at which temperature a constant weight is obtained in from a half to one hour.

THE USE OF COTTON AS A FILTER.

BY A. B. CLEMENCE.

IN the estimation of silicon in pig irons a large portion of the time is taken in filtering off the silicon and graphite, especially in irons rich in silicon. If a filter pump is not at hand, and a filter paper only is used, three hours are often taken for filtering and washing a solution that contains 3 or 3.5 per cent of silicon, and even when a pump is used, in which case a support must be used, the filtering is often tedious.

Having had occasion some time since to estimate the silicon in a large number of samples of iron rich in silicon, I looked for a quick filtering material, and in cotton I believe I have found all that can be desired.

The method of analysis is the "Sulphuric Acid Method" with, perhaps, some slight modifications.

One gram of the borings are placed in a 6" evaporating dish and 40 c. c. of a mixture of 1 part concentrated sulphuric acid and 5 parts nitric acid of 1.20 sp. gr. are added. A watch

glass is placed on the dish and set on an iron plate heated by a 6-inch multiple burner.

The dish may be left without care until the iron is dissolved and evaporated till the ferric sulphate has spattered on to the watch glass. Water is now added and boiled for 2 or 3 minutes when it is ready to filter.

The filter is made as follows: A 3-inch filter paper is folded as usual and the apex cut off leaving a hole about $\frac{1}{8}$ inch in diameter ; a wad of cotton (the absorbent cotton of the druggists) is pressed into the apex and, when wet, may be either with a pump or by the mouth, pressed tight enough to hold the residue. Even without a pump this filter will run so fast that close watching will be needed to keep the funnel full. Wash as usual with hot dilute hydrochloric acid and with hot water when the residue, cotton and paper, is ready for the weighed crucible. Burning with a blast lamp completes an estimation in 40 minutes from the time of weighing the borings. The weight of the ash of the cotton will of course vary with the amount used, while that of the paper will be the same in each case, but it never need be more than .0005 gram, and this small amount may be disregarded when working on silicons for Bessemer charging.

WORCESTER STEEL WORKS, WORCESTER, }
MASS., March, 1887. }

A HYDROCARBON BLOW-PIPE AND FURNACES.

By WM. HOSKINS.

Chemists and Assayers familiar with solid fuel furnaces are aware of the many inconveniences and annoyances attending their use. A gas furnace, if a good one, is entirely satisfactory where gas is available ; but in small towns, mining camps, and other places where it cannot be obtained, the want of a portable, clean, and economical apparatus has long been

felt. I am aware of no *effective* liquid fuel furnace now in the market. Any furnace requiring a bellows to produce a blast is certainly very inconvenient. The furnace illustrated, I think, meets the requirements as nearly as is possible, being portable, automatic, cleanly and economical. The fuel required is gasoline of 74 degrees.

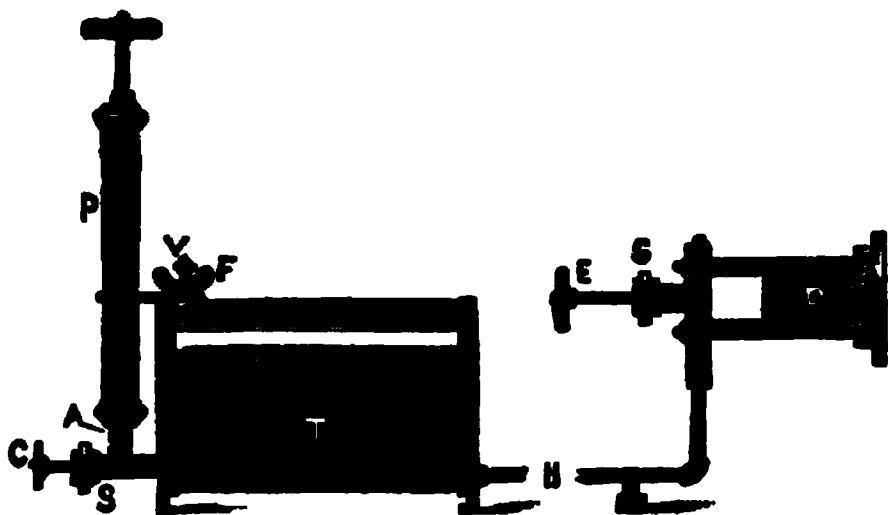


Figure 1.

Figure 1.—T is a tank made of brass and holding about one gallon of the liquid fuel (gasoline). P an ordinary force pump with automatic valve and cut off at A and C, V a little thumb screw for letting out the air when

through an operation. F is the filling screw. The burner D is of course the principal part of the apparatus. The two sides and end are hollow permitting the fluid to circulate around the burner; when about to use the apparatus this is heated by burning a little alcohol or gasoline in a dish under it.

The valve C is now opened and a few strokes of the pump given and the valve closed, thus creating a pressure in the tank on *top* of the gasoline, which is forced through the pipe H to the burner, through the lower tube, across the head and back again through the upper tube and out at the fine orifice at the end of E, but the liquid as it passes through the hot burner becomes vaporized and issuing from it as a highly heated gas, mixes with the air and burns as is seen in the large engraving Fig. 4; if the pressure in the tank be now increased the fluid flows faster and the vapor issues with great force from the burner, drawing in the surrounding air and burning as a very hot *blast*. The heat produced by the combustion which takes place in the central tube of the burner is sufficient to continue the vaporization in the small tubes and so the operation becomes automatic after once starting; it is only necessary to use the pump occasionally (once every half hour

or so) to keep up the pressure in the tank which is lessened only by the consumption of the fuel, no air passing out from the tank into the tube H. The fire may be controlled by regulating with the valve E, or by varying the pressure, which in ordinary work should be about twenty pounds per square inch.

The blast may be used in various ways besides heating crucibles, &c. Figure 2

is a crucible furnace, and Figure 3 is a muffle furnace especially designed for this apparatus. The blast

enters at the back; complete combustion takes place in a long

Fig. 2.

Fig. 3.

slightly tapering combustion chamber from which the hot products of combustion are conveyed around the muffle, issuing from a narrow opening at the top of the furnace. As to the capacity, one-half pound of cast iron can be melted in fifteen to twenty minutes, and the muffle furnace can be made sufficiently hot for assaying in about ten minutes.

The blow-pipe apparatus weighs about 10 pounds, crucible

furnace is 4 inches in diameter, and 5 inches deep, and is constructed of fire clay. The muffle furnace is also fire clay and will receive a muffle 10 inches long, 6 inches wide by 4 inches high.

Figure 4.

It might be well to add that the cost of operating in our larger cities where gasoline can always be obtained is about 3 cents per hour.

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THE CHEMISTRY OF TYROTOXICON, AND ITS ACTION UPON THE LOWER ANIMALS.

BY VICTOR C. VAUGHAN, M. D., PH. D.,

Professor of Physiological Chemistry in the University of Michigan.

SINCE making my report on the investigations concerning the nature of tyrotoxicon*, I have continued my work, aided greatly by Messrs. F. G. Novy and E. V. Riker. We soon ascertained that if some butyric acid ferment be prepared as is ordinarily done in the preparation of butyric acid, and some of this be added to normal milk, and the whole be kept in closely stoppered bottles for eight or ten days, the poison will be developed in the milk in considerable quantity. The milk should be filtered, the filtrate neutralized with sodium carbonate, and then extracted with ether.

Having a strong solution of the poison in absolute alcohol which had been obtained from milk inoculated as stated above, I added to it some platinum chloride and began to evaporate on the water-bath. As soon as the alcohol evaporated the residue exploded with great violence. The vessel, a glass evaporating dish, was broken into fine fragments and these were scattered over the room; while the gas-light under the water-bath was extinguished. The experiment was repeated a number of times with like results. From some of this alcoholic solution the platinum was removed with hydrogen sulphide gas; but the filtrate was then found to have lost its explosive property. This reminded us that diazobenzol compounds form with platinum chloride a highly explosive compound and that diazobenzol is also decomposed by hydrogen sulphide. Some diazobenzol nitrate was prepared according to the method of Griesst†, and comparisons made between this and tyrotoxicon.

With equal parts of sulphuric acid and carbolic acid the prepared diazobenzol nitrate gave a green coloration; while with the same reagents, tyrotoxicon gave a color which varied from a yellow to an orange-red. But the diazobenzol nitrate

*This Journal, vol. I, page 24, et seq.

†Annalen der Chemie und Pharmacie, B. 137, S. 39

dissolved in the whey of normal milk, and extracted with ether or in the presence of other proteids, gave the same shades of color as the tyrotoxin did, and, the potassium compound of tyrotoxin prepared by the method to be given later produced the same shade of green as did the artificial diazobenzol. This color test may be used as a preliminary test in examining milk for tyrotoxin. It is best carried out as follows: place on a clean porcelain surface two or three drops each of pure sulphuric acid and pure carbolic acid. This mixture should remain colorless or nearly so. Then add a few drops of the aqueous solution of the residue left after the spontaneous evaporation of the ether. If tyrotoxin be present, a yellow to an orange-red color will be produced. This test is to be regarded as only a preliminary one; for it may be due to the presence of a nitrate or nitrite*. The tyrotoxin must be purified according to a method to be given farther on before the absence of nitrate or nitrite can be positively demonstrated.

In the filtrate from milk which is rich in tyrotoxin, after neutralization with sodium carbonate, filtration and acidifying with hydrochloric acid, gold chloride produces a precipitate, which is insoluble in water; but soluble in hot alcohol, from which it separates on cooling in golden plates, which are more or less imperfect. Diazobenzol compounds give with gold chloride a precipitate having all these properties. In both cases the gold compound is decomposed by frequent treatment with hot alcohol, and this fact prevented any satisfactory ultimate analysis of this salt. It should be remarked here that from some samples of milk this gold salt is obtained much more easily than from others, and the difference is dependent not so much upon the amount of tyrotoxin present, as upon the condition of the other organic matter present. It is best obtained from samples which have stood in well stoppered bottles for a month or longer.

Tyrotoxin obtained from milk was treated according to the method recommended by Griess† for the preparation of diazobenzol potassium hydrate, and the per cent. of potassium

*The coloration with nitrates and nitrites is darker than with diazobenzol.

† *Annalen der Chemie und Pharmacie*, B. 137, S. 54.

in the compound obtained was determined. The filtrate from the milk which had been inoculated with the ferment and kept in a stoppered bottle in a warm room for 10 days, was neutralized with sodium carbonate, agitated with an equal volume of absolute ether, allowed to stand in a stoppered flask for 24 hours, the ether removed and allowed to evaporate from an open dish. The aqueous residue was acidified with nitric acid, then treated with an equal volume of a saturated solution of potassium hydrate and the whole concentrated on the water-bath. On being heated the mixture became yellowish-brown and emitted a peculiar aromatic odor. Both the color and the odor corresponded exactly with the color and odor produced by carrying some of the artificial diazobenzol through a comparative test. On cooling, the mass crystallized, the resulting compound appearing in the test with the tyrotoxicon and in the comparative test also, in beautiful, six-sided plates, along with the prisms of potassium nitrate. The crystalline mass obtained from the tyrotoxicon was treated with absolute alcohol, filtered, the filtrate evaporated on the water-bath, the residue dissolved in absolute alcohol, from which it was precipitated in a white crystalline form with ether. The precipitate was collected, washed with ether, dried, and the per cent. of potassium estimated as potassium sulphate.

.2045 gram of the substance yielded .109 gram of potassium sulphate.

Per cent. of potassium calculated in $C_6H_5N_2OK$ 24.42 ; found 23.92. This analysis establishes the identity of tyrotoxicon and diazobenzol.

Chemists will now appreciate the great difficulty that has been experienced in isolating the active agent of poisonous cheese. The readiness with which diazobenzol decomposes is well known. When warmed with water it breaks up into carbolic acid and nitrogen. Hydrogen sulphide decomposes it; therefore, all attempts to obtain the poison by precipitating it with some base, such as mercury or lead, and then removing the base with hydrogen sulphide, have failed. Moreover, diazobenzol is only a transition product of putrefaction.

I have frequently found that leaving some milk rich in the

poison in an open beaker for 24 hours would be sufficient to destroy the whole of the poison.

We know nothing positively concerning the acid with which diazobenzol is combined in the milk or cheese. We prepared some diazobenzol butyrate, $C_6H_5N_2C_4H_7O_2$, and ascertained that the crystals of this compound correspond with those of tyrotoxicon and that they decompose in moist air with the same rapidity. This is the first time that diazobenzol has been found as a product of putrefaction, and it is possible that many of its allied compounds may be formed in the same way.

The following experiments will show that the effects of tyrotoxicon and diazobenzol upon the lower animals are identical:

Experiment 1. From one-half gallon of some milk, which had stood in a tightly stoppered bottle for three months, there was obtained quite a concentrated aqueous solution of the poison after the spontaneous evaporation of the ether. Ten drops of this placed in the mouth of a small dog three weeks old caused within a few minutes frothing at the mouth, retching, the vomiting of frothy fluid, rapid breathing, muscular spasm over the abdomen, and after some time watery stools. The next day the dog seemed to have recovered partially; but was unable to retain any food. This condition continuing for two days, the animal was killed with chloroform. No examination of the stomach was made.

Experiment 2. Tyrotoxicon obtained from poisonous ice-cream was given to a cat. Within ten minutes the cat began to retch and soon it vomited. The retching and vomiting continued for two hours during which time the animal was under observation, and the next morning it was observed that the cat had passed several watery stools. After this, although the cat could walk about the room, it was unable to retain any food. Several times it was seen to lap a little milk, but on doing so it would immediately begin to retch and vomit. This condition continuing, after three days the animal was placed under ether, and its abdominal organs examined. We certainly expected to find marked inflammation of the stom-

ach ; but we really did find the stomach and small intestines filled with a frothy, serous fluid, such as had formed the vomited matter, and the mucous membrane very white and soft. There was not the slightest redness anywhere along the alimentary canal.

Experiment 3. Some tyrotoxicon obtained from milk which had been inoculated with poisonous cream and allowed to stand for forty-eight hours was administered to a large, old cat. It soon produced retching, but no vomiting or diarrhoea. The amount of the poison administered in this case was small.

Experiment 4. Some tyrotoxicon from milk was given to a young, but full-grown cat. Within fifteen minutes there was marked and evidently painful retching, and within half an hour vomiting accompanied by rapid breathing. Later there were several stools, the first two of which contained fecal matter ; but the subsequent ones were rice-water like and wholly free from fecal odor. After two days some more of the poison was given, and the vomiting and diarrhoea again induced. The animal was then anesthetized, and an examination of the stomach and intestine showed the mucous membrane blanched as was found in experiment 2.

We have the records of a number of other experiments with tyrotoxicon on the lower animals ; but as the symptoms induced in all were substantially the same, it is unnecessary to note them here. We will now give the effects observed in the lower animals after the use of the prepared diazobenzol.

Experiment 5. Gave to a large, old cat, 100 milligrams of diazobenzol butyrate. Immediately the animal began to purge. Then she lay upon the floor breathing rapidly and retching severely for two hours, when she died. The retching was most violent, but vomiting seemed impossible. Post-mortem examination showed the lungs greatly congested, but the mucous membrane of the stomach and intestine was not reddened. The stomach contained some food. We suppose that the congestion of the lungs was due to the violent retching and to the feeble action of the heart.

Experiment 6. To a young but full-grown Maltese cat we gave 100 milligrams of diazobenzol butyrate. With most violent retching, but without either vomiting or stool, the animal died within thirty minutes after the administration of the poison. The lungs were found acutely congested and the stomach free from any redness. The circular fibres of the small intestine were tightly contracted.

Experiment 7. Gave to a full-grown cat 25 milligrams of diazobenzol butyrate. Within ten minutes vomiting and purging were induced. The first stools contained fecal matter; but the subsequent ones were like rice-water and wholly free from fecal odor. After two days the cat was able to take food, then 10 milligrams more of the poison was given, with the reproduction of the vomiting and purging. The animal then rapidly emaciated, and after a few days, it was anesthetized and the mucous membrane of the stomach and intestine found blanched. The lungs were not congested.

Experiment 8. 10 milligrams of the poison produced profuse diarrhoea and continued vomiting in a cat.

Experiment 9. 75 milligrams produced vomiting and diarrhoea with congestion of the lungs in a dog.

It seems unnecessary to detail any more of these experiments, as the identity of tyrotoxicon with diazobenzol is now established, not only by chemical analysis, but this proof is strengthened, if chemical analysis can be strengthened, by the action of the poison on the lower animals and by post-mortem appearance.

We think it highly probable that diazobenzol or some closely allied substance will be found in all those foods, which from putrefactive changes, produce nausea, vomiting and diarrhoea. In some oysters, which produced these symptoms, I have recently found tyrotoxicon.

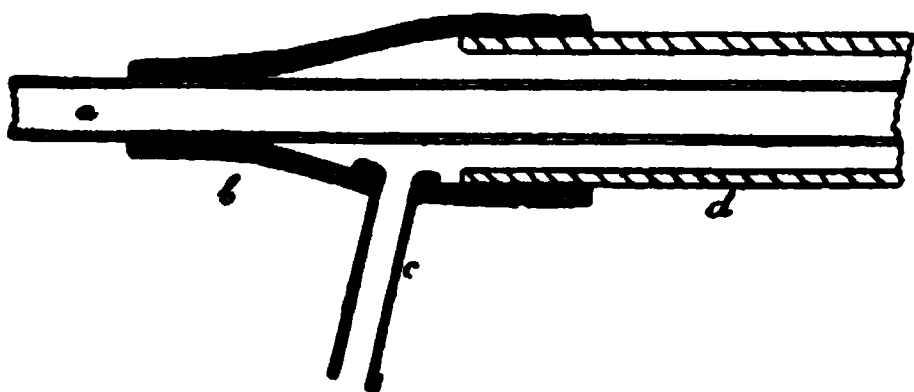
Milk or other fluid to be tested for this poison should be kept in well stoppered bottles; for if the fluid be exposed to the air, the tyrotoxicon may decompose in a few hours. The filtrate from the milk or the filtered aqueous extract of cheese should be neutralized with sodium carbonate, then shaken

with half its volume of pure ether. Time should be given for the complete separation of the ether. Purified tyrotoxin is insoluble in ether, and it probably owes its solubility in ether at this stage to the presence of impurities. After complete separation the ether should be removed with a pipette and allowed to evaporate spontaneously from an open dish. The residue from the ether may be dissolved in distilled water and again extracted with ether; but repeated extractions with ether are to be avoided, for as the tyrotoxin becomes purified, it becomes less soluble in ether. To a drop of an aqueous solution of the ether residue apply the preliminary test with sulphuric and carbolic acids. To the remainder of the aqueous solution of the ether residue add an equal volume of a saturated solution of caustic potash, and evaporate the mixture on the water-bath. The double hydrate of potassium and diazobenzol will be formed if tyrotoxin be present, and this may be recognized by its properties and reactions which have already been described.

A NEW FORM OF LIEBIG'S CONDENSER.

BY EDWARD HART.

Two years ago Prof. S. P. Lattimore described to me a form of condenser which I have used ever since. Prof. Lattimore told me that he had the idea from Prof. Caldwell, of Cornell, with whom he believed it originated. I have never seen it described and find it so valuable that I think it should see the light. The accompanying cut, shows one end of the condenser. *a* is the inner and *d* the outer tube connected by



means of thick, vulcanized, rubber tubing. *c* is a glass tube for carrying off the water; the opening in the tube through which this is inserted is made

with the smallest size cork-borer and the tube then forced in.

The advantages of this form of condenser are its simplicity, efficiency and cheapness. The flexibility of the tube *c*, which in the ordinary form is easily broken, is also a great advantage.

THE DECOMPOSITION OF BLAST FURNACE CINDER BY ACID.

By J. E. MERION AND EDWARD HART.
(Continued from page 163.)

The silica in the following chilled cinders has been determined by the fusion and the acid methods.

DURHAM, APRIL 6.*

	(1)	(2)
Acid Method	34.32	34.26
Fusion Method	34.29	34.41

EDGAR THOMSON.

Acid	30.96	30.98
Fusion	30.76	30.81

LEWISTOWN, CHARCOAL—(Cold Blast.)
(First sample.)

Acid	37.10	37.01
Fusion	36.89	36.97

(Second sample.)†

Acid	39.45	39.53
Fusion	39.27	39.38

LUCY, EASTON, PA.

Acid	40.23	40.29
Fusion	40.31	40.41

KEYSTONE, EASTON, PA.

Acid	40.1	40.05
Fusion	40.24	40.18

BARNESTON, CHESTER CO., PA.—(Cold Blast Charcoal).
(First sample.)

Acid	51.03	50.89
Fusion	50.85	50.67

*At this time the furnace was running on high phosphorus pig.
†At the time these samples were taken the furnace was not doing well and the manager intended blowing out.

(Second sample.)			
Acid	50.38		50.29
Fusion	50.28		50.34
*CHARCOAL CINDER. (Source not known.)			
Fusion	46.87	Acid	46.98

A number of other determinations have been made but it is sufficient to say that in every cinder so far examined the two methods give results equally close.

The following letter has been received since the publication of the first part of this article :

NEWARK, N. J., MAY 5, 1887.

PROF. EDWARD HART, EASTON, PA.—*Dear Sir* : In the last number of the JOUR. ANAL. CHEM. you have an article on the "Decomposition of Blast Furnace Cinder by Hydrochloric Acid." I can add an example in which the method has worked well. For several years I have decomposed the cinder from our Spiegel furnaces by cold concentrated hydrochloric acid. The samples are taken by dipping a ladle of cinder from the run, the ladles are made of iron about half an inch thick, and form a cake of cinder about four inches in diameter and three quarters of an inch thick in the center curving to a sharp edge ; with our cinder this makes the cake vitreous throughout. It is completely decomposed by hydrochloric acid provided care is taken that the gelatinous silica formed does not cover and protect particles of cinder. I have tried to decompose the cinder by nitric acid for rapid manganese determinations, but the results were not satisfactory. The cinder has as a rule the general formula $2\text{RO}, \text{SiO}_2$ and contains SiO_2 30 to 38 per cent., Al_2O_3 8 to 13 per cent., FeO 1 to 3.5 per cent., MnO 9 to 15 per cent., CaO 23 to 33 per cent., and MgO 6 to 13 per cent.

Yours truly,

GEORGE C. STONE.

In a letter from Mr. R. H. Lee, Jr., accompanying the sample of cinder from Lewistown, he says :

"I think you will find that all coke and charcoal furnace cinders can be easily and entirely decomposed by HCl , provided they are pulverized finely enough and care taken to stir frequently, to prevent the undecomposed portions from being covered with gelatinous silica. At least all coke cinders I have had any experience with will do so."

* USE OF THE GOOCH CRUCIBLE.

We find that results can be obtained much more rapidly with the use of the Gooch crucible. Care must however be taken to get a compact felt, otherwise silica runs through and the results are low. Satisfactory determinations can be made in half an hour, including weighings, in this way.

With the return of cooler weather we intend to prepare a number of artificial cinders in order to learn how much silica must be added before the product becomes insoluble in acid.

We wish to express our thanks to Messrs. F. Firmstone, F. H. Knight, G. Convers, B. F. Fackenthal, Jr., W. H. Blauvelt, R. H. Lee, Jr., Wm. M. Potts and James Gayley for samples and suggestions.

*This cinder had been chilled by pouring into water.

THE ESTIMATION OF QUININE BY KERNER'S METHOD.

BY EDSSEL A. RUDDIMAN.

WITHIN the past few years unusual attention has been given to the examination of the sulphate of quinine for the other alkaloids which occur with it in cinchona barks, more especially cinchonidine. In this examination, the method of Dr. Kerner, first published in 1862, has been adopted by the pharmacopœias of Germany, France, and the United States. The pharmacopœia of Great Britain adopts the first principle of Kerner's test—the removal of the excess of quinine by its crystallization as sulphate—and then resorts to separation of free alkaloids by ether. Notwithstanding the general and official use of Kerner's operation, to fix the quality of a medicinal agent of the first importance, this method is still open to questions of criticism, questions to be answered only by a course of investigation. The work undertaken by the writer has been devoted to determinations as follows :

(1) As to the effect of an initial digestion of the medicinal sulphate of quinine in water at 100°C., followed by the digestion at 15°C., in comparison with results obtained by digesting at once at 15°C.

(2) As to the effect of variations in the temperature of the liquid during titration on the amount of ammonia necessary to redissolve the precipitate, filtration being always done at 15°C.

(3) As to the accuracy of Kerner's figures for the amount of ammonia water, sp. gr. 0.920, required to dissolve 1 milligram of cinchonidine sulphate.

(4) A proposed modification of the method for the quantitative estimation of cinchonidine sulphate in quinine sulphate.

(5) On the amount of water which should be taken in applying Kerner's test to salts of quinine other than the sulphate.

(1) THE EFFECT OF DIGESTING MEDICINAL QUININE SULPHATE AT DIFFERENT TEMPERATURES.—In an article published in 1877, Paul¹ called attention to the fact that, in the application of Kerner's test for the detection of cinchonidine sulphate in quinine sulphate, all of the cinchonidine is not dissolved. Since then, and more especially within the last few months, several writers as Paul², Yungfleisch³, the committee for the revision of the French Codex⁴, Hesse⁵, Kerner⁶, and others have acknowledged that there is truth in this statement. The reason given is that, in the manufacture, the sulphates of quinine and cinchonidine crystallize together. The amount of water of digestion being insufficient to dissolve all of the quinine, the cinchonidine is not all dissolved. The French Codex now directs that the digestion take place in hot water, while Yungfleisch advises that the temperature of the water used be 100°C. This undoubtedly makes the test far more severe, but even at 100°C. there is an insufficient amount of water to dissolve all of the quinine.

In testing the commercial salt I have made a modification of the U.S. Ph. method, and in so doing, have attempted to make it such that, on an average, those samples of quinine which are included by the officinal test will be included by this modification, and those samples which are excluded by the officinal test will be excluded by this modification. It is as follows: Take 1 gram of the salt and dissolve in 30 c. c. of boiling water (this being enough to dissolve it), cool and digest at 15°C. for two hours and filter. To 5.26 c. c.* of the filtrate add 7 c. c. of water of ammonia, sp. gr. 0.960, and a clear solution should be obtained. To determine the amount of filtrate which should be taken, I proceeded as follows: 1 gram of the salt was digested with 10 c. c. of water at 15° for three hours and filtered. To 5 c. c. of the filtrate, ammonia water, sp. gr. 0.960 was added from a burette until the precipitate was just redissolved and the amount† used was noted.

1. See list of references at the end of this paper.

* Or, what is equivalent, 5 c. c. of the filtrate may be taken and 6.65 c. c. of water of ammonia added.

† If the temperature of the resulting solution was above or below 15°C. due allowance was made. See page 295.

1 gram of the same sample was dissolved in 30 c. c. of boiling water, the solution cooled, digested at 15°C. for three hours and filtered. To 5 c. c. of the filtrate, ammonia was added as before and the amount used was noted. From these figures, the required amount of filtrate of the sample digested at 100°C. may be calculated.* Twelve experiments as follows were made with samples of quinine from three manufacturers. Experiments I, II, and III were made upon the same sample; experiments IV, V, and VI on a sample from a different manufacturer; experiments VII, VIII, and IX on one sample, and X, XI, XII on another sample from a third manufacturer.

<i>No. of Experiment.</i>	<i>No. of c.c. of ammonia required for 5 c. c. of filtrate after digesting 1 gm. of the salt in 10 c. c. of water at 15° C.</i>	<i>No. of c.c. of ammonia required for 5 c. c. of filtrate after digesting 1 gm. of the salt in 30 c.c. of water at 100° C.</i>	<i>Proportion.</i>
I	7.1	8.8	8.8 : 7.1 :: 5:x=4.03
II	7.2	9.4	9.4 : 7.2 :: 5:x=3.83
III	6.6	7.9	7.9 : 6.6 :: 5:x=4.19
IV	8.9	8.5	8.5 : 8.9 :: 5:x=5.23
V	9.5	9.1	9.1 : 9.5 :: 5:x=5.21
VI	9.5	9.05	9.05 : 9.5 :: 5:x=5.24
VII	12.2	8.5	8.5 : 12.2 :: 5:x=7.17
VIII	10.9	7.9	7.9 : 10.9 :: 5:x=6.89
IX	11.3	8.2	8.2 : 11.3 :: 5:x=6.90
X	7.5	7.9	7.9 : 7.5 :: 5:x=4.74
XI	7.6	7.8	7.8 : 7.6 :: 5:x=4.87
XII	7.4	7.5	7.5 : 7.4 :: 5:x=4.93

I found the average result of these twelve experiments to be 5.26 c. c. This figure may, however, be varied by further experiment, and in fact the amount varies for each sample. The variation depends upon the condition in which the cinchonidine sulphate exists. It may be deposited largely on

*The proportion is : The amount of ammonia used for the 5 c. c. filtrate from sample digested at 100° : amount of ammonia used for 5 c. c. filtrate from sample digested at 15° :: 5: x.

the outside of the crystals of quinine sulphate, due to the incomplete separation of the mother liquor, in which case it will be easily dissolved; or, it may be crystallized throughout with the quinine sulphate.

(2) THE EFFECT OF THE TEMPERATURE OF TITRATION UPON THE AMOUNT OF AMMONIA TAKEN.—In applying the U.S.Ph. test to a sample of quinine sulphate, I observed that portions of the same filtrate, indicated that the salt should be included or excluded by the test, according to the temperature of the liquid after filtration. On having the temperature of the room such that the resulting mixture should be very nearly at 15° C., a distinct turbidity was formed on adding 7 c. c. of water of ammonia (sp. gr. 0.960) to 5 c. c. of the filtrate, while if the temperature of the titrated liquid rose to about 25° C., a clear solution followed. To determine the exact effect of the temperature during titration upon the amount of ammonia required, I proceeded as follows: The standard quinine sulphate* was prepared from Böhringer's quinine sulphate by adding the calculated amount of sulphuric acid necessary to convert it into the bisulphate, which was dissolved in hot water nearly to saturation and cooled. The crystals were then drained and dried by means of bibulous paper and a press. They were dissolved a second time and dried in a similar manner. The quinine bisulphate was then converted into the normal sulphate by adding a solution of sodium hydrate to neutralization.

The crystals were twice dissolved in hot water, cooled, dried between filter paper and a third time dissolved in hot water, cooled and allowed to effloresce.† The solution was made by digesting the standard quinine sulphate in water at the ordinary temperature, then reducing it to 15° C. for two hours and filtering at the same temperature. The ammonia

*Various methods for the purification of quinine sulphate have been given. See KERNER, *Zeitsch. anal. Chem.*, xx, 150; PRESCOTT, *Pro. Am. Pharm. Asso.*, 1878, p. 828; DAVIES, *Pharm. Jour. Trans.*, [3] xvi, 358; HESSE, *Pharm. Jour. Trans.*, [3] xvi, 818.

†In all my experiments where standard quinine sulphate was used, it was prepared in the same manner.

solution was standardized* by titrating it with a normal solution of oxalic acid, using the table of percentage and specific gravity given in the U.S.Ph. 1880.

Regulating the temperature of the room so that it was near the temperature at which I wished to titrate, I proceeded as follows: 10 c. c. of the standard quinine sulphate solution were measured into a small globe-shaped flask by means of a pipette and ammonia water was added from a burette to within 1 c. c. of the quantity required to dissolve the precipitate first formed. The flask was then closed with a stopper and inverted once. More ammonia was added, a few drops at a time, and afterwards drop by drop. After each addition the flask was closed, inverted and allowed to stand a few seconds, taking for the whole titration four to five minutes. Immediately after the precipitate was redissolved the temperature of the solution was taken. Bringing together all the titrations made at the same degree of temperature, about 10 titrations having been made for each degree, I found the average titer of ammonia for each degree between 14° and 26° C. inclusive, as given in the table below. The extremes of temperature, 14° and 26°, were chosen since they are about the limits of ordinary temperature. Finding the difference of titer between each degree and the one next above it, I took the average of these differences to represent in general the decrease of ammonia required for the increase of each degree of the centigrade thermometer. When ammonia water of sp. gr. 0.920 is used, the general average of all the differences is found to be 0.148 c. c., but for ammonia water sp. gr. 0.960 the general average is 0.172 c. c.

Then to obtain the correct amount of ammonia water, sp. gr. 0.920, necessary to redissolve the precipitate at 15° C., there must be added to the amount of ammonia used 0.148 c. c.

*In all cases where ammonia was used, it was standardized by titrating with oxalic acid. For sp. gr. 0.920 ammonia percentage 21.8 was used; for sp. gr. 0.960 percentage 9.8 was employed. These data are from the table of CARIUS, U. S. Ph., p. 425. According to the observations of A. B. LYONS, *Proc. Mich. Phar. Asso.*, p. 189, the 21.8 per cent. corresponds to sp. gr. 0.92119; and the 9.8 per cent. corresponds to 0.96170 (water at 40 C. = 1, and temp. obs. 150 C.

TEMPERATURES	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°
<i>No. of c. c. of ammonia water sp. gr. 0.920 necessary for 10 c. c. of quinine solution.</i>	7.4	7.2	7.1	6.8	6.8	6.9	6.6	6.4	6.1	6.0	5.9	5.7	5.4
	7.4	7.1	7.1	6.8	7.1	6.7	6.7	6.8	6.1	6.0	5.7	5.5	5.6
	7.4	7.5	7.8	6.7	7.0	6.8	6.8	6.5	6.1	5.9	5.8	5.6	5.5
	7.3	7.2	7.8	7.2	6.8	6.7	6.8	6.8	6.2	6.0	5.9	5.7	5.5
	7.2	7.5	7.0	7.4	6.5	6.6	6.4	6.4	6.1	5.8	6.0	5.7	5.6
	7.3	7.3	7.1	7.0	6.7	6.4	6.2	6.4	6.1	5.8	6.0	5.8	5.6
	7.2	7.2	7.1	7.1	6.7	6.6	6.2	6.4	6.1	5.9	6.1	5.8	5.6
	7.4	7.0	6.9	7.0	7.0	6.4	6.4	6.4	6.1	5.9	5.8	5.8	5.4
	7.2	7.1	6.9	7.0	6.5	6.4	6.4	6.4	5.9	5.7	6.0	5.4	
		7.3		6.6	6.7	6.5	6.3	6.3	6.2	5.8	5.6		
		7.2		6.7	6.5	6.4	6.2	6.2	6.2				
				6.8		6.4		6.1	6.1				
General average of differences for one degree=0.148 c. c.													
Average.	7.31	7.23	7.08	6.92	6.67	6.56	6.38	6.32	6.10	5.88	5.88	5.66	5.54
TEMPERATURES	14°	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	
<i>No. of c. c. of ammonia water sp. gr. 0.960 necessary for 10 c. c. of quinine solution.</i>	10.5	10.6	10.5	10.2	10.1	9.9	9.9	9.6	9.5	9.0	9.1	9.2	
	10.5	10.6	10.4	10.4	10.0	9.9	9.6	9.6	9.1	9.3	9.1	8.8	
	10.7	10.3	10.8	10.2	10.2	9.6	9.6	9.6	9.1	9.2	8.8	8.6	
	10.6	10.3	10.1	10.8	9.8	9.7	9.8	9.5	9.4	9.4	9.0	9.1	
	10.6	10.2	10.5	10.1	10.1	9.8	9.7	9.6	9.5	9.2	8.9	8.9	
	10.4	10.3	10.3	10.8	10.1	9.9	9.9	9.4	9.3	9.4	9.1	8.6	
	10.5	10.4	10.1	10.8	10.2	9.7	9.5	9.6	9.3	9.0	9.0	8.7	
	10.8	10.2	10.1	10.1	9.9	10.0	9.8	9.3	9.0	9.1	9.2	8.9	
	10.5	10.6	10.4	10.3	10.0	10.2	9.5	9.6	8.8	9.2	8.7	8.8	
	10.8	10.1	10.3	10.3	10.1	10.0	9.5	9.1	9.0		9.0	8.7	
	10.4				9.8	9.5		9.3	9.2		9.0		
					10.2	9.6							
Average	10.63	10.36	10.3	10.25	10.04	9.90	9.78	9.52	9.31	9.15	8.99	8.83	
General average of differences for one degree=0.172 c. c.*													

*It appears that of ammonia water of sp. gr. 0.960, there are required only 1.5 times more than of the water of sp. gr. 0.920, though the latter is 2.2 times stronger than the former.

for every degree of increase of temperature of titration. If ammonia water of sp. gr. 0.960 be used, then 0.172 c. c. must be added for every degree.

(3) EXPERIMENTS TO DETERMINE THE ACCURACY OF KERNER'S FIGURES.—For the quantitative estimation of cinchonidine sulphate in quinine sulphate by his ammonia test, Kerner⁷ gives figures obtained for the fraction of 1 c. c. of water of ammonia, sp. gr. 0.920, which 1 mg. of cinchonidine requires to dissolve it, varying from 0.288 to 0.350 c. c. His method of experimentation in brief is as follows: To 50 c. c. of standard quinine sulphate solution, prepared by digesting chemically pure quinine sulphate in water at 15° C. and filtering, he adds a weighed quantity of cinchonidine sulphate, varying the amount added. This solution, in portions of 10 c. c., is then titrated with ammonia water of sp. gr. 0.920. Simultaneously with this, 50 c. c. of the standard solution are titrated in portions of 10 c. c. each. The excess of ammonia used in the former case over that used in the latter is divided by the number of milligrams of cinchonidine sulphate contained in 10 c. c. of the former solution. This will give the amount of ammonia water necessary to dissolve 1 milligram of the cinchonidine salt. According to this method, I made twenty-five experiments as given below, varying the amount of cinchonidine sulphate from 0.005 gram to 0.05 gram for every 50 c. c. of the standard solution.

Three experiments (I, VIII, XIII) were made to find the number of c. c. of the ammonia water taken by the standard quinine sulphate filtrates alone. This number of c. c. was deducted from the reading in each following experiment with cinchonidine addition, thus: the 6.385 c. c. obtained in I, was deducted from the readings in experiments II to VII, for the calculations to give the figures of the last column.

In each experiment I took the average of four titrations; then taking the average of the twenty-five experiments, covering one hundred titrations, I found that for every milligram of cinchonidine there was required 0.360 c. c. of ammonia water of sp. gr. 0.920 to dissolve the precipitate. In the fol-

lowing experiments the temperature of the resulting solution of each titration was taken as soon as the titration was completed. When the temperature thus taken varied from 15° C., due allowance was made by adding or subtracting, for every degree of increase or decrease, as the case might be, 0.148 c. c. to or from the amount of ammonia used. In order to secure constancy in composition of the cinchonidine salt taken, the cinchonidine sulphate was exposed to the air until thoroughly effloresced and then weighed as having the formula $(C_{19}H_{23}N_2O)_2H_2SO_4 \cdot 2H_2O$. From this the equivalent quantity of the crystallized salt ($6H_2O$) was calculated. The following abbreviations are used in the table below: S. Q. S. for standard quinine sulphate solution; am. for ammonia water; ef. cin. sulph. for effloresced cinchonidine sulphate.

<i>No. of the Experiment.</i>	<i>To 50 c. c. of S. Q. S. add of ef. cin. sulphate.</i>	<i>No. of c. c. of am. for 10 c. c. of the quinine solution.</i>	<i>Temp'ture of each titration when made.</i>	<i>Average No. of c. c. of am. used, at 15° C.</i>	<i>1 mg. of cryst cinchonidine sulph. takes of ammonia.</i>
I {		6.1	16°	6.385	
		6.3	"		
		6.2	"		
		6.2	"		
		6.3	"		
		6.2	"		
		6.3	"		
		6.3	"		
II {	.00454 gm.	6.3	18°	6.744	.359 c. c.
		6.4	"		
		6.2	"		
		6.3	"		
III {	.00454	6.3	18°	6.746	.360
		6.7	16°		
		6.4	17°		
		6.25	18°		

<i>No. of the Experiment.</i>	<i>To 50 c. c. of S. Q. S. S. add of ef. cin. sulphate.</i>	<i>No. of c. c. of am. for 10 c. c. of the quinine solution.</i>	<i>Temp'ture of each titration when made.</i>	<i>Average No. of c. c. of am. used, at 15°C.</i>	<i>1 mg. of cryst cinchonidine sulph. takes of ammonia.</i>
IV {	.01354	7.1	18°	7.444	.353
		7.2	"		
		6.9	"		
		6.8	"		
V {	.01354	6.9	18°	7.444	.353
		7.1	"		
		7.0	"		
		7.0	"		
VI {	.01818	7.5	17°	7.845	.368
		7.6	"		
		7.5	"		
		7.5	18°		
VII {	.02275	8.0	17°	8.232	.369
		7.8	18°		
		7.8	"		
		7.7	"		
VIII {		6.1	15°	6.140	
		6.2	"		
		6.0	16°		
		5.9	"		
		5.9	17°		
		5.7	18°		
		5.7	"		
		5.7	"		
IX {	.00454	6.3	17°	6.491	.351
		6.2	16½°		
		6.25	16°		
		6.4	16°		
X {	.00909	6.8	15°	6.750	.305
		6.7	"		
		6.7	"		
		6.8	"		

THE ESTIMATION OF QUININE.

299

<i>No. of the Experiment.</i>	<i>To 50 c. c. of S. Q. S. S. add of ef. cin. sulphate.</i>	<i>No. of c. c. of am. for 10 c. c. of the quinine solution.</i>	<i>Temp'ture of each titration when made.</i>	<i>Average No. of c. c. of am. used, at 15° C.</i>	<i>1 mg. of cryst cinchonidine sulph. takes of ammonia.</i>
XI {	.00909	6.8	16°	6.82	.340
		6.7	"		
		6.6	"		
		6.6	"		
XII {	.01354	6.9	16°	7.112	.324
		7.2	15°		
		7.1	"		
		7.1	"		
XIII {		6.6	15°	6.50	
		6.3	"		
		6.4	"		
		6.65	"		
		6.4	"		
		6.65	"		
		6.6	"		
		6.6	"		
		6.3	"		
		6.5	"		
XIV {	.01354	7.0	15°	7.0	.388
		7.0	"		
		7.0	"		
		7.0	"		
XV {	.01818	8.1	15°	7.975	.368
		8.0	"		
		7.9	"		
		7.9	"		
XVI {	.01818	7.9	15°	7.975	.368
		8.0	"		
		8.1	"		
		7.9	"		
XVII {	.02275	8.3	15°	8.3	.360
		8.4	"		
		8.2	"		
		8.3	"		

<i>No. of the Experiment.</i>	<i>To 50 c. c. of S. Q. S. S. add of ef. cin. sulphate.</i>	<i>No. of c. c. of am. for 10 c. c. of the quinine solution.</i>	<i>Temp'ture of each titration when made.</i>	<i>Average No. of c. c. of am. used, at 15°C.</i>	<i>1 mg. of cryst cinchonidine sulph. takes of ammonia.</i>
XVIII {	.02275	8.4 8.3 8.3 8.2	15° " " "	8.3	.360
XIX {	.02727	8.4 8.8 8.8 8.5	15° " " 16°	8.662	.360
XX {	.02727	8.7 8.6 8.8 8.8	15° " " "	8.725	.370
XXI {	.03182	9.3 9.2 9.1 8.9	14½° 15° " "	9.106	.372
XXII {	.03182	9.1 9.2 8.9 9.0	16° " " "	9.198	.385
XXIII {	.03637	9.6 9.2 9.4 9.4	15° " " "	9.375	.359
XXIV {	.03637	9.6 9.4 9.4 9.3	15° " " "	9.450	.368
XXV {	.04191	9.7 9.9 9.9 9.9	16° 15° " "	9.877	.376

<i>No. of the Experiment.</i>	<i>To 50 c. c. of S. Q. S. S. add of ef. cin. sulphate.</i>	<i>No. of c. c. of am. for 10 c. c. of the quinine solution.</i>	<i>Temp'ture of each titration when made.</i>	<i>Average No. of c. c. of am. used, at 15°C.</i>	<i>1 mg. of cryst cinchonidine sulph. takes of ammonia.</i>
XXVI {	.04191	9.8	15°	9.8	.366
		9.8	"		
		9.9	"		
		9.7	"		
XXVII {	.04546	10.2	16°	10.324	.382
		10.3	"		
		10.3	15°		
		10.2	"		
XXVIII {	.04546	10.3	15°	10.336	.383
		10.3	"		
		10.2	17°		
		10.1	16°		

Taking the average result of the twenty-five experiments, I found that 1 milligram of cinchonidine sulphate, $[(C_{19}H_{23}N_2O)_2, H_2SO_4, 6H_2O]$ when dissolved in a solution of quinine sulphate, requires 0.36 c. c. of ammonia water of sp. gr. 0.920 to precipitate and redissolve it.

(4) METHOD FOR QUANTITATIVE ESTIMATION.—Kerner's method and claims for the quantitative estimation of cinchonidine sulphate in commercial quinine sulphate are here given in a faithful translation as follows: Five grams of the salt to be examined are rubbed in a mortar with distilled water to a homogeneous mass, then transferred to a stoppered flask, rinsing with enough water so that in all 50 c. c. are used. The mixture is then either placed in water (of about 50°C.) shaken vigorously and cooled—or digested without heating for 12 to 18 hours, shaking vigorously and frequently. The flask is now placed in cold water, together with the mixture of standard quinine and water for comparative titration, and the ammonia water, and when all are at the same temperature the quinine solutions are filtered through dry filter papers. The temperatures of the air and water taken into consideration in the operation lie between 12° and 24°. For the absolute numerical titer, they are not indifferent, but for the relative result they

are. The preservation of a fixed low temperature is not necessary, if the standard quinine solution is prepared and filtered at the same temperature. As a measuring instrument for the ammonia, a long burette finely divided (1-20 c. c.) is used. The saturated quinine sulphate solution is measured with an exact 10 c. c. pipette into a test-glass, and the titration is carried on as follows: 5 c. c. of ammonia water are added from the burette to 10 c. c. of the quinine solution, the test-glass then closed with the finger and gently turned two or three times without shaking. The greater part of the quinine is now precipitated and redissolved but the fluid is still distinctly turbid. The ammonia is now added in small portions (3-10, 2-10, 1-10 c. c.) and each time, after gently turning, it is observed whether complete clearing follows or not. On each addition of the ammonia, it is well to wait five to ten seconds before adding more. After some experience, the end reaction—the complete clearing up of the solution—may be discerned with great accuracy. If 5 grams of the sulphate are treated with 50 c. c. of water, and 40 c. c. filtrate be obtained, there will be sufficient to make four titrations, of which the average result may be taken. The simultaneous titration of the standard quinine solution gives the exact titer of ammonia, and the excess used over this to obtain the solution of the quinine sulphate under examination, indicates the amount of cinchonidine present more exactly than is determined by any gravimetric method. As seen from the analytical results (Kerner's) 0.288 c. c., or in round numbers 0.3 c. c., of ammonia water sp. gr. 0.920 corresponds to one milligram of crystallized cinchonidine sulphate in one gram of the sulphate of quinine tested. And as the possible mistake in observation amounts to only 0.1 c. c. or at the highest 0.15 c. c., closer readings could hardly be wished for than those of the titration method, while an error of more than 1.30 per cent. to 1.20 per cent. does not need to happen. It is to be observed that the examination of only the quinine sulphate which passes the definition of the official test, or rather that which does not contain more than 1-1.5 per cent. of cinchonidine sulphate is taken into consideration. If an aqueous mixture in the proportion of 1:10 be prepared

from a sulphate of quinine containing more than 2 per cent. of cinchonidine sulphate, the estimation is inaccurate, because the filtrate then contains so large a proportion of foreign alkaloïds that the end-reaction is obscured. The addition of the ammonia in such a case causes either a large flaky precipitate difficult to redissolve, or, during the addition of ammonia near the point of clarification, a greater turbidity suddenly occurs so that on standing it becomes gelatinous and on that account the end-reaction is not distinct. This inconvenience is entirely avoided, if, after noting the kind and intensity of the turbidity by the qualitative test, either the 1: 10 prepared mixture is diluted with a definite amount of standard quinine solution, or, if a higher proportion of water be used in the preparation of the saturated solution, 1 part of the salt to 50, 100, 200, etc., parts of water.*

Mention has been made of the fact that, by digesting commercial quinine sulphate in 10 parts of water at 15° C., the cinchonidine sulphate is not all dissolved. Now since by digesting it at a warmer temperature the filtrate indicates a higher per cent. of cinchonidine, to estimate as nearly as possible the amount of cinchonidine, all of the quinine should be dissolved. It seems then as though Kerner's method of estimation should be modified so that all of the salt shall be dissolved. This may be done by digesting the quinine sulphate in 30 parts of water at 100°, cooling, digesting at 15° for two hours, and filtering. To portions of the filtrate apply the test as given by Kerner. In calculating the amount of cinchonidine sulphate, allowance must be made for the dilution caused by using 30 c. c. instead of 10 c. c. of water for digestion. It is not claimed that all of the cinchonidine is estimated by this method, for no doubt some of it crystallizes out again with the quinine. Hesse says that two crystallizations are necessary to remove all of the cinchonidine, while others maintain that four or five crystallizations are necessary.

In working with one sample of commercial quinine sul-

*This report of Dr. Kerner, in 1880, is presented at length because it does not appear to be accessible in our language.

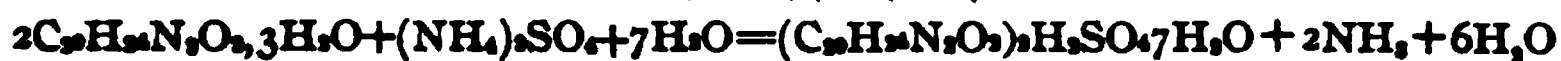
phate, I estimated the amount of cinchonidine sulphate according to Kerner's method and found the indication to be 1.2 per cent. In using the same proportion of the salt and water, but by digesting at 100° then cooling, digesting at 15° and filtering, on adding ammonia water, the end-reaction could not be determined accurately on account of the gelatinous precipitate which forms when there is much over 2 per cent. of cinchonidine sulphate present. Now on treating a portion of the same sample with 30 parts of boiling water, cooling, digesting at 15° , filtering and applying the test, it indicated 6.3 per cent. of cinchonidine sulphate present in the quinine sulphate.

In working with a sample of quinine sulphate made by another manufacturer, according to Kerner's method of estimation, that is by digesting the salt with 10 parts of water at 15° , the result indicated 2.2 per cent. cinchonidine. When the same salt was digested with 30 parts of boiling water before applying the test to the filtrate, an indication of 5.9 per cent. of cinchonidine sulphate was obtained.

(5) ON THE AMOUNT OF WATER WHICH SHOULD BE USED IN THE APPLICATION OF KERNER'S TEST TO SALTS OF QUININE OTHER THAN THE SULPHATE.—Dr. Prescott⁹ called my attention to the fact that, in the U.S.Ph. application of Kerner's test to the salts of quinine other than the sulphate, the proportion of ten parts of water to one part of *the sulphate formed*, is not retained. By thus varying the proportion of water, the stringency of the test is subjected to variation. Following are equations showing the amount of water which should be used, if the proportion in the original test of Kerner be preserved. Dr. Lyons has also called my attention to the fact that in the U. S. Ph. test for quinine sulphate itself the original proportions are departed from, inasmuch as the weighed amount of the crystallized salt is dried before treatment with the water. Therefore, the proportions of water calculated below must be multiplied, by the factor 0.878, to bring them to the proportions of the U. S. Ph. test for the sulphate. The factor 0.878 is based upon the averages of

Henry B. Parsons, in 1884, giving 13.84 per cent. water as the mean quantity in 1015 samples from 100-ounce cans just opened.

FOR THE FREE ALKALOID.



756

126

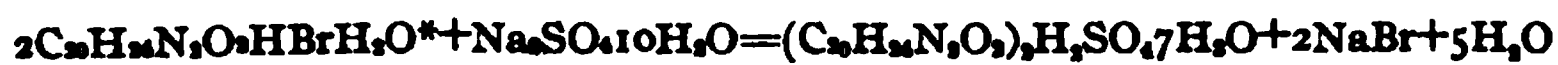
872

$$756 : 872 :: 1 : X = 1.1534 \quad 1.1534 \times 10 = 11.534$$

$$756 : 126 :: 1 : X = .166 \text{ (after evaporation on water-bath, and then adding water, } 7H_2O \text{ taken up)}$$

$$11.534 + .166 = 11.700 \quad 11.7 \text{ c. c. of water to be added to 1 gram of the alkaloid.}$$

HYDROBROMIDE.



845.6

872

90

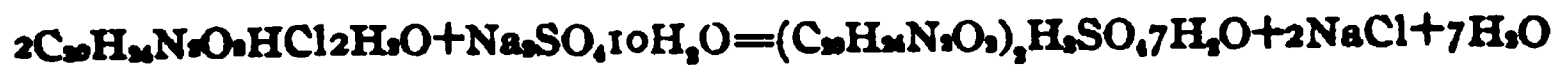
$$845.6 : 872 :: 1 : X = 1.0312 \quad 1.0312 \times 10 = 10.312$$

$$845.6 : 90 :: 1 : X = .106 \text{ (correction for water of crystallization)}$$

$$10.312 - .106 = 10.206 \text{ c. c. of water to be added to 1 gram of hydrobromide}$$

$$15.309 \text{ c. c. of water to be added to } 1\frac{1}{2} \text{ gram of hydrobromide.}$$

* The authority for giving the hydrobromide of quinine as having but one molecule of water of crystallization is found in the French Codex, p. 148, and in Ladenburg's Handwörterbuch, I, 250.

HYDROCHLORIDE.¹⁹

788.8

872

126

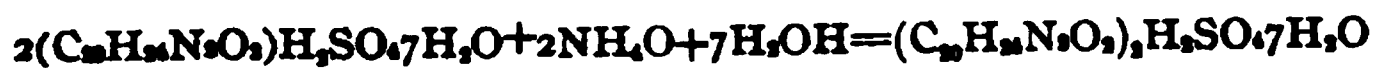
$$788.8 : 872 :: 1 : X = 1.1054 \quad 1.1054 \times 10 = 11.054$$

$$788.8 : 126 :: 1 : X = .159 \text{ (water of crystallization)}$$

$$11.054 - .159 = 10.895 \text{ c. c. of water to be added to 1 gram of hydrochloride}$$

$$16.342 \text{ c. c. of water to be added to } 1\frac{1}{2} \text{ gram of hydrochloride.}$$

BISULPHATE.



1096

126

872

$$1096 : 872 :: 1 : X = .7956 \quad .7956 \times 10 = 7.956$$



$$1096 : 126 :: 1 : X = 1.114 \text{ (water of crystallization)}$$

$$7.956 + 1.114 = 3.07 \text{ c. c. of water to be added to 1 gram of bisulphate.}$$

The U.S.Ph. test of the free alkaloid is more stringent than for the sulphate, since it directs that for every 10 c. c. of water, there shall be sufficient alkaloid used to make 1.1534 gram of the sulphate. In case of the hydrochloride or the hydrobromide the test is considerably more severe, first, because an insufficient amount of water is used, and second, because in the conversion of the hydrochloride or hydrobromide into the sulphate, direction is made to use hot water. In testing the bisulphate, the officinal method directs that, to the mixture of the salt and water, ammonia be added to neutralization and then sufficient water added to make the mixture measure 10 c. c. This is to be criticised for two reasons: first, because it does not take into account the fact that 1 gm. of the bisulphate forms only .7956 gm. of the normal sulphate, and second, because there is no allowance made for the space occupied by the salt, and the proportion of water added to the sulphate formed varies inversely with the volume of the salt. To 1 gm. of the bisulphate of quinine as tested in the U.S.Ph., there should be added in all (taking into consideration the water of ammonia) 8.07 c. c. of water.

In applying the U.S.Ph. tests to the salts of quinine other than the sulphate, some difficulty¹⁰ has been experienced in obtaining the required 5 c. c. filtrate. Various methods have been offered to obviate the difficulty, but the one proposed by C. N. Lake¹¹ seems to be the one which the most nearly corresponds to the original test. It is to increase both the amount of salt and of water yet preserving the proportion between them. Working with the free alkaloid, I found, in using the ratio of water to the alkaloid as directed in the officinal test, by taking $1\frac{1}{2}$ times as much as there stated, the required 5 c. c. filtrate could be obtained with a little difficulty, but doubling the amount no difficulty was experienced. By taking $1\frac{1}{2}$ gms. of the alkaloid and 17.5 c. c. of water, which is in the proportion of 10 parts of water to 1 part of the sulphate formed, the 5 c. c. of filtrate can be easily obtained. With the hydrochloride and hydrobromide I had no difficulty by taking the amount of the salt and water as directed in the pharmacopœia. Since the amount of water which *should* be used is

greater than the amount which is used, there was of course no difficulty when the correct amount was taken. In case of the bisulphate, the required amount of filtrate may be obtained either by doubling the amounts directed in the pharmacopœia or by taking $2\frac{1}{2}$ gms. of the salt and the theoretical amount of water which is 20.09 c. c.

CONCLUSIONS.—(1) The pharmacopœial test of commercial quinine sulphate, when applied as there directed, does not, as a rule, correctly indicate the amount of cinchonidine sulphate present. By using a higher temperature and water sufficient to dissolve all of the salt, a closer approximation to the real amount of cinchonidine contained therein may be obtained.

(2) The temperature of the resulting liquid at the time the titration is completed has a considerable effect upon the amount of ammonia water necessary to redissolve the precipitate. For every degree that the temperature of the titration is above 15° , there should be added 0.148 c. c. to the number of c. c. of ammonia water of sp. gr. 0.920 used.

(3) In my experiments I found that 0.36 c. c. of water of ammonia, sp. gr. 0.920, is necessary to precipitate and redissolve 1 milligram of cinchonidine sulphate, i. e. in the quantitative estimation of cinchonidine sulphate in quinine sulphate, every 0.36 c. c. of ammonia used in titrating the 10 c. c. of filtrate from the sample being tested, over that used in titrating the 10 c. c. of filtrate from the standard quinine, indicates 1 mg. of cinchonidine sulphate in 1 gram of the sulphate of quinine tested, or 0.1 per cent.

(4) In estimating the cinchonidine sulphate in commercial quinine sulphate, to get a result nearest correct, it is necessary to dissolve the salt. This can be done by using a temperature of 100° C. and 30 parts of water; if more water be used the temperature need not be so high, but while the amount of impurities remains about as found at present 30 parts of water will be sufficient.

(5) The proportion of water to the sulphate in the officinal test of the forms of quinine is not precisely the same as in Kerner's original test. If the proportion in the latter case be retained, there should be used for 1 part of the free alka-

loid 11.7 parts of water; for the bisulphate 8.07 parts of water; for the hydrochloride 10.895 parts of water; and for the hydrobromide 10.2 parts of water. Also for the dried sulphate 10.144 parts of water.

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UNIVERSITY OF MICHIGAN, CHEMICAL LABORATORY, June, 1887.

THE SEPARATION OF NICKEL AND COBALT FROM IRON.*

BY J. B. MACKINTOSH.

As all chemists know, the separation of these metals is, at best, a long and tiresome task. It is generally assumed that two or at most three precipitations of the iron as basic acetate, or as hydrate by ammonia are sufficient to effect a perfect separation, thus obtaining all the nickel and cobalt in the filtrates. I have found, however, in cases where there is a comparatively large amount of these metals present, as in most meteoric irons, that it is sometimes necessary to repeat the precipitation five or six times or even oftener before the filtrates cease to react for nickel and cobalt. In the analysis of one meteoric iron I noticed the very interesting fact that after all the nickel had been removed, cobalt still remained with the iron, although the amount of cobalt in the sample was not more than one-tenth that of the nickel. At the time when this was noticed the color of the filtrate on concentration was pink, having previously been green; if I remember correctly this took place at about the sixth time of precipitation.

The probable reason for the difficulty seems to be, that the nickel and cobalt become partially peroxidized, and possibly in the case of cobalt that some of the ammonia-cobalt bases are formed, which are either rather insoluble or are decomposed, with formation of peroxide, upon boiling.

In order to decrease the time and the number of operations necessary, I tried the old method of precipitation of all three metals from the boiling solution with ammonium sulphide, with subsequent treatment with hydrochloric acid. I thus obtain two portions, the precipitate containing nearly all the cobalt and nickel with very little iron, and the solution con-

* School of Mines Quarterly, July 1887. From an advance sheet sent by the author.

taining nearly all the iron with very little nickel and cobalt; both these portions are then treated separately in the usual way by precipitation of the iron as basic acetate, and a perfect separation may be much more readily obtained, than if the solution had been treated directly without this preliminary concentration.

I tested this method on two meteoric irons which I have recently analyzed,* and determined the amounts of combined nickel and cobalt found in the two portions after one precipitation as sulphides and also after three such precipitations. It is to be noted that these operations take very little time, as the precipitated sulphides of nickel and cobalt are easily filtered and washed, and also that the bulk of solutions treated is very small, so that the time occupied by these three precipitations, will hardly exceed that occupied by one basic acetate precipitation, and certainly will not when the time necessary for the concentration of the filtrate is taken into consideration. The results obtained are as follows:

PRECIPITATION OF THE BOILING SOLUTION WITH AMMONIUM SULPHIDE AND
SUBSEQUENT SOLUTION IN DILUTE HYDROCHLORIC ACID.

	Total Ni + Co present.	Fe present.	Per cent. Ni + Co. in precipitate—in filtrate.	
One precipitation, . .	0.0956	1.0266	92.08 per cent.	7.92 per cent.
Three precipitations, .	0.1248	0.6021	96.32 "	3.68 "

In the first case the nickel and cobalt amount to 8.52 per cent. of the total weight of metals, and in the second case to 17.17 per cent.

* American Journal of Science, March 1887, pp. 225, 232.
LEHIGH UNIVERSITY, South Bethlehem, Pa.

A NEW FORM OF BUNSEN BURNER.

BY F. P. VENABLE.

IN using gas prepared from gasoline for heating purposes in the laboratory, I have been much troubled by the smoky flame given by the ordinary burner when fresh gasoline is in the generator. This is due to the larger amount of light hydrocarbons present at that time and to the decreased pressure.

For the complete combustion of the gas, then, it is necessary to increase the proportion of oxygen admitted to secure a good flame, the pressure must be greater and a fine draught insured.

Since devising this modification of the Bunsen burner, I have had no difficulty in the use of the carburetted air. The Springfield gas machine in use is a small one, holding about three barrels, and we pay careful attention to the specific gravity of the gasoline used and to the weight of the stone which runs the fan, thus securing the best results.

The burner presents so many advantages in its use however that I have thought it advisable to draw attention to it as a good form also for laboratories where coal gas is at command.

The accompanying cut will illustrate the points of difference between this and the old form of burner. The main feature is that the supply of gas is regulated at the base of the burner by a milled wheel and that this supply is diminished only at the issuing jet inside the chimney.

The advantages are: 1st. An easy and convenient mode of regulating the supply of gas, independent of the regulation of the air.

2nd. The screw motion gives a means of securing a gradual and accurate decrease or increase of flame.

3rd. As the gas is checked in its flow only at the issuing jet there is but little diminution of pressure, which for the use of gasoline gas is a very essential point. It enables one to secure a very small and still colorless flame.

4th. This burner is a very powerful one.

This burner has proved very satisfactory in the laboratory

here, and very favorable reports of it have been received from laboratories using coal-gas where it has been tried. The burner is manufactured by Gilbert & Barker Manufacturing Company, of New York.

UNIVERSITY OF NORTH CAROLINA, 1887.

NOTE ON A NEW TEST FOR IRON.

BY F. P. VENABLE.

A solution of cobalt nitrate to which strong hydrochloric acid has been added, is blue. It was noticed that when some impure hydrochloric acid was used a green color was gotten instead of the blue. This change was traced to the iron in the acid, and as I have seen no mention of it elsewhere, I venture to give the present notice of this test. It is very simple, rapid and delicate for detecting traces of iron and is especially useful in testing strong acids. The delicacy of the test is such that when even $\frac{1}{100,000}$ of a gram of a ferric salt are added to the blue strongly acid solution mentioned above, the green is clearly given. With a somewhat larger amount this green is quite vivid. If too much of the ferric solution is used the cobalt solution becomes pink from the addition of water. The test is not given by ferrous salts, nor does the presence of ferrous salts interfere with it. I have thought that the green was due to the addition of yellow ferric chloride to blue cobalt solution. Other yellow solutions which I have tested failed however to give the green.

University of North Carolina, 1887.

ABSTRACTS.

APPARATUS AND REAGENTS.

New Thermoregulator.—L. Rügheimer, Ber. d. dent. chem. Ges. 20, 1280. The gas passes in at *g* and out through *h*, which is connected with the burner. *b* contains mercury, *e* is a narrow glass tube connected by stout rubber tubing with the air bulb shown in fig. 3. In using the apparatus the air bath is heated nearly to the desired temperature, *d* being open.



Then *d* is closed and the mercury rises in *b*, covers the end of *f* and shuts off all the gas except that passing through the small opening *i*. It is easy by means of this apparatus to keep the temperature in the air bath so that it does not vary more than one degree, if the air thermometer is large enough. The tube *f* should be ground off so that *p*, fig. 2, = $\frac{1}{2} n$, and the tubes *f* and *b* be of such size that the area of *o* is equal to the area of *m—n*. If the tube *b* is drawn out as shown in fig. 4 it may be used with a smaller air ther-

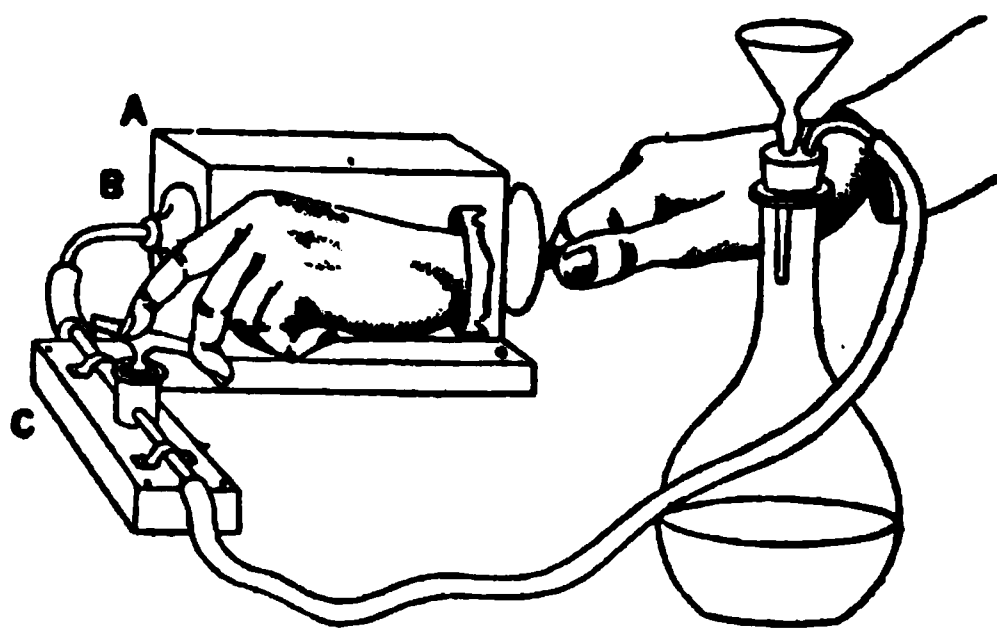
mometer, the narrower part of the tube having a correspondingly small tube *f*.

Apparatus for Electrolytic Work.—Robert V. Malapert, *Zeit. anal. Chem.* **26**, 56. Apparatus for making several electrolytic determinations at the same time.

Gas Balance.—Friederich Lux, *Zeit. anal. Chem.* **26**, 38. For determining the specific gravity of gases.

Some Pieces of Chemical Apparatus.—Woodville Latham, *Amer. Chem. Jour.* **9**, 142.

Simple, Portable, Quick Filtering Apparatus.—This is in-



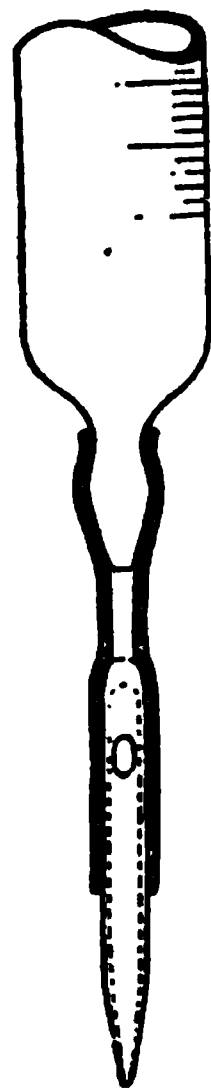
tended for use in the absence of a head of water for running a Bunsen pump. *B* is a hard rubber syringe fastened to a block *A*, and worked with the right hand. *C* is a three-way cock

worked with the left hand.

Sulphuretted Hydrogen Apparatus Without Stray Fumes.—Sulphide of iron is placed in the upper bulb of a Kipp's apparatus, the stem having first been filled with broken porcelain. The bottom globe and half of the middle one are filled with dilute acid. To the middle globe, through the tubulure, a cork, tube and pinch cock are fastened; by blowing through this the acid is forced into the upper bulb. When the gas is no longer needed the pinchcock is opened and the acid falls into the lower bulbs.

Simple Arrangement for Reverse Filtration. (Carmichael's Plan).—"The neck of an ordinary vial is cut off. The outer end is ground on a lead, copper or wooden surface with emery and water. Into the other end a one-hole rubber stopper is inserted and pushed in so as to be flush with the opposite end. On the last mentioned end a perforated platinum disk and a disk of moistened filter paper are placed. Into the hole of the rubber stopper a tube is inserted which is itself connected with the aspirator."

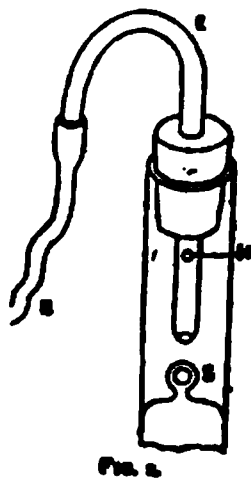
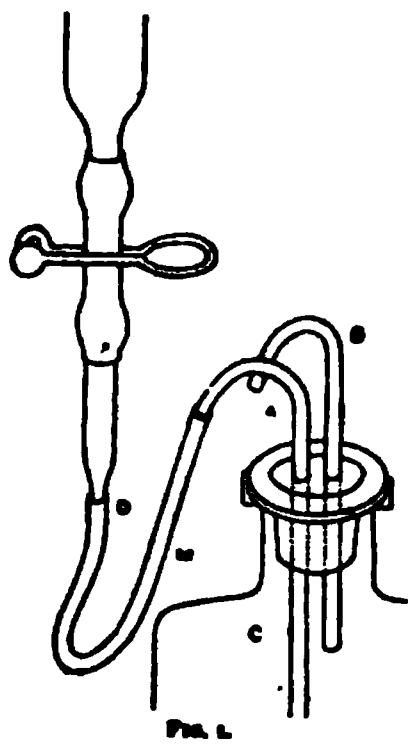
New Jet for Burettes.—W. Leybold, Zeit. anal. Chem. **26**, 230. Many chemists use a short bit of glass rod placed inside the rubber tube instead of a pinchcock. The author proposes to combine this with the jet as shown in the figure. By pressing the rubber tube between the finger and thumb a narrow channel forms, through which the liquid passes into the jet through the side opening.



Method for Obtaining Chlorine from Bleaching Powder with Kipp's Apparatus.—Clemens Winkler, Ber. d. deut. chem. Ges. **20**, 184. Good bleaching powder is mixed with $\frac{1}{4}$ its weight of gypsum, moistened slightly with water and the mass formed into cubes by pressure. These cubes when dried are placed in a Kipp's apparatus and acted upon by hydrochloric acid. A regular supply of chlorine can be conveniently obtained in this way.

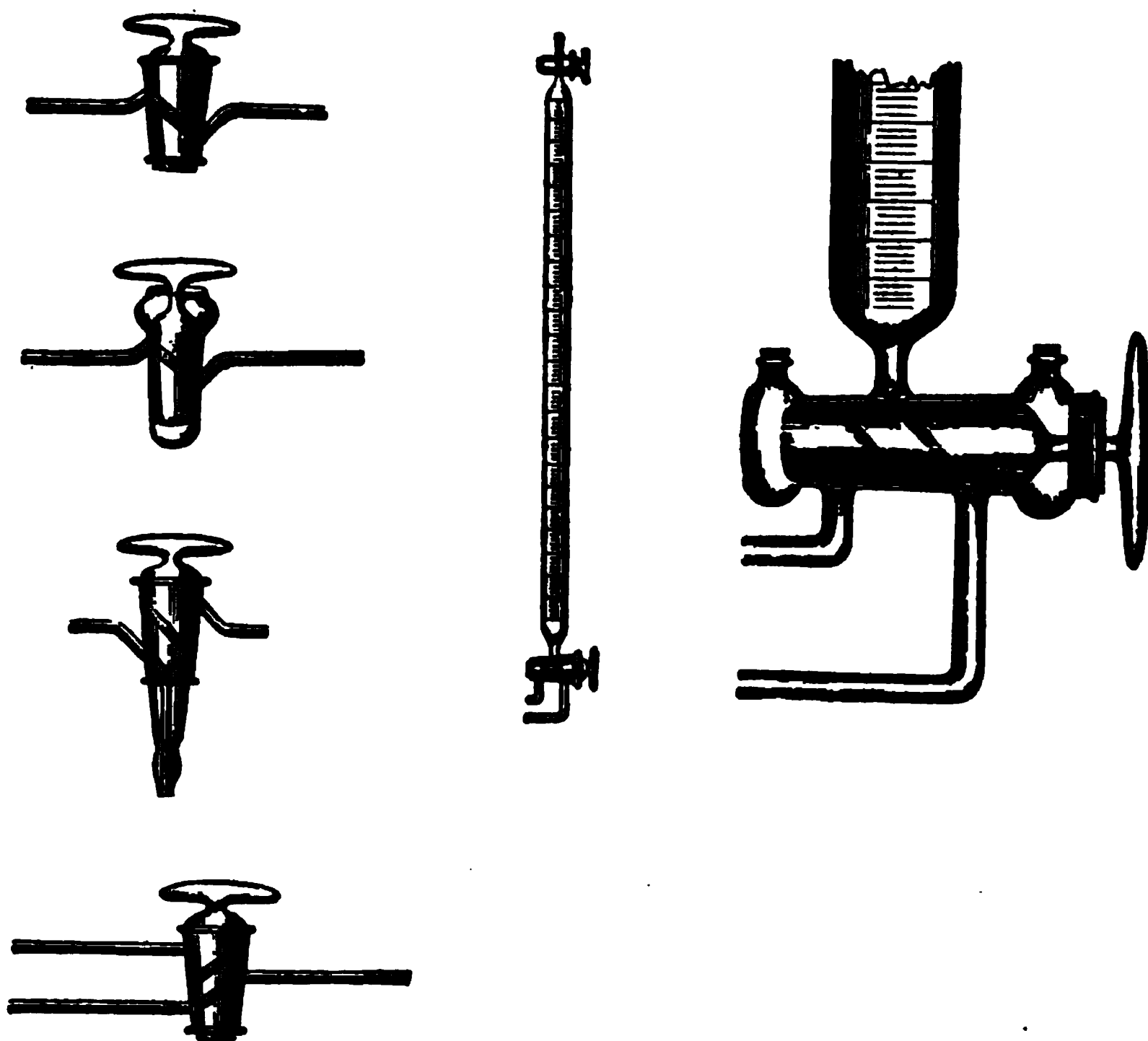
To Clean Burettes.—Carl Mohr, Chem. Zeit. **11**, 510, fills them with a tolerably strong solution of potassium permanganate and allows them to stand for one or two days. The solution is then run out and the burette washed out with dilute hydrochloric acid and water.

Apparatus for Filling a Burette.—C. L. Penny, Amer. Chem. Jour. **9**, 141. The tube *A* reaches to the bottom of the bottle while *B* just passes through the cork. When not in use the end *D* of the rubber tube *M* is slipped over *B* to prevent evaporation. To fill the burette *D* is slipped over the tip and suction applied at *N*. The tube *E* is closed at the lower end and has a side opening *H*. When the top of the swimmer strikes the lower end of the tube *E*



any air bubbles under it pass up around the sides and escape.

New Glass Stop-Cocks.—Greiner and Friederichs, *Zeit. anal. Chem.* 26, 48, have described some new forms of glass ap-



paratus. Especially noteworthy among these are some new forms of stop-cocks, shown in the cut. These need no description. Their value to the chemist is evident at a glance.

Laboratory Fittings.—John Gibson, *Jour. Soc. Chem. Ind.* 6, 205. A description of the ventilating arrangements and desk fittings in use in the new chemical laboratories of the University of Edinburgh. The article is fully illustrated and should be read in full.

Convenient Method for Obtaining Pure Sulphuretted Hydrogen—R. Fresenius, *Zeit. anal. Chem.* 26, 339, has applied the plan of Winkler, described above, to the preparation

of a continuous supply of pure (arsenic free) sulphuretted hydrogen. Calcium sulphide, prepared by igniting a mixture of gypsum, charcoal and rye flour is mixed with calcined gypsum in the proportion of four parts of the former to one of the latter. The mixture is made into a paste with water and fashioned into cubes, which are placed in a Kipp's apparatus and treated with hydrochloric acid.

Preparation of Metallic Chlorides.—Lothar Meyer, Ber. d. deut. chem. Ges. **20**, 681, has succeeded in preparing chlorides of aluminum, magnesium, etc., by passing a mixture of an indifferent gas and carbon tetrachloride over the oxide, contained in a porcelain tube and exposed to the heat of a Glaser's furnace.

In place of carbon tetrachloride, H. N. Warren (Chem. News, **55**, 192) uses petroleum saturated with chlorine or hydrochloric acid.

A New Method for Standardizing Iodine Solutions.—W. Kalmann, Ber. d. deut. chem. Ges. **20**, 568. If iodine is added to sodium sulphite hydriodic acid and sodium sulphate are formed :



A measured volume of the iodine solution is placed in a beaker and the solution of sodium sulphite run in from a burette until it loses all color. Methylorange is then added and the hydriodic acid determined by $\frac{1}{2}$ alkali. The sodium sulphite used is the ordinary commercial salt and the solution is made by dissolving about 15 gms. in a liter of water.

An iodine solution containing 0.008483 gms. iodine per c. c. gave the following figures :

Iodine solution c. c.	Alkali c. c.	= Iodine gms.	In 1 c. c. iodine = gms. iodine.
20	14.65	0.016928	0.008464
30	22.05	0.025476	0.008492
40	29.4	0.033972	0.008493
40	29.4	0.033972	0.008493

For Filtering Precipitates which run up the side of the funnel, A. Gawalovski, Zeit. anal. Chem. **20**, 51, uses filters

whose edges have been dipped in melted wax, paraffine or fat. The substance used must leave no ash when burned.

The Use of Solid Bromine in Dissolving Sulphides.—A. Brand, Zeit. anal. Chem. 20, 222. The so called "solid bromine" is made by saturating cylindrical pieces of infusorial earth with bromine. These cylindrical pieces are made by mixing the infusorial earth with less than 1 per cent. of lime or alkali and the mixture fritted together after molding—like a Dinas brick. The pieces are made of two sizes, the smaller having a diameter of 7 mm. and containing about 1 gm. bromine per cm. of length, and the larger of 15 mm. and containing 3 gm. bromine per cm. of length.

The sulphide is placed in a boat and inserted in a tube, one end of which is bent at a right angle and connected with nitrogen bulbs containing a mixture of bromine water and hydrochloric acid. To prevent fumes of bromine from annoying the operator the second nitrogen bulb is connected with a vessel containing shavings moistened with alcohol. The boat is placed near the bend of the tube; behind it are placed sticks of the solid bromine and the tube is closed with a stopper of gypsum and a cork. The gypsum stopper protects the cork from the action of the bromine. On heating the boat and that part of the tube containing the bromine the sulphide is attacked and converted into bromide.

Indicators in Volumetric Analysis.—R. T. Thomson, Jour. Soc. Chem. Ind. 6, 195. The author, in former papers, has reported upon the behavior of litmus, methylorange, phenacetolin, phenolphthalein, rosolic acid and lacmoid as indicators. He has now extended his observations to turmeric, cochineal dimethylamidoazobenzene and congo red.

Turmeric seems to be useless as an indicator in presence of ammonia, showing only about 97 per cent. of the amount present, and is useless in presence of ammonium compounds; in this respect it resembles phenolphthalein. It can, however, be employed, as turmeric paper, in estimating the acid in colored solutions of acetic, tartaric, oxalic, lactic and succinic

acids, but cannot be substituted for phenolphthalein in estimating the saponification equivalent of oils. It may be used in the form of red brown paper for detecting small amounts of acid dissolved in strong alcohol, a property not possessed by litmus paper.

Cochineal is entirely useless in presence of organic acids. Salts of iron and alumina cause the pink color, slightly modified, to remain after the addition of excess of acid.

Dimethylamidoazobenzene behaves like methylorange in every respect and is in every way inferior to it as an indicator.

Congo Red has been proposed as an indicator for free acid in alum, but the author finds that it is incapable of detecting 0.2 per cent. of free acid or even of giving a trustworthy indication of the presence of 0.5 per cent. of free sulphuric acid in alum.

“Of the ten indicators which we have been considering the three representative ones are of primary importance. So far as the results of my experiments show, all the good and serviceable qualities required of indicators are held in comparatively greater perfection by methyl orange, phenolphthalein and litmus than by the other seven. The only exception to this is in the neutralization of sulphurous acid to normal sulphite of ammonium by the aid of rosolic acid, for which purpose all the remaining indicators are valueless. Litmus is the only one of those selected from which satisfactory papers can be prepared, and the advantage of having these as well as solution cannot be doubted. In nearly every particular lacmoid paper, blue and red, is an excellent substitute for methyl orange, and may be employed in colored solutions, where the last named indicator would be useless. The solution, however, is not so good, as it is slightly affected by weak acids, such as carbonic and boric, but the papers I find to be quite as effective as methyl orange in these and similar cases. Turmeric papers, yellow and red brown, may be used in place of phenolphthalein, chiefly in the titration of weak organic acids; but there are many circumstances in which it is inadmissible.”

TABLE SHOWING THE BASICITY OF ACIDS WITH DIFFERENT INDICATORS, WHEN TITRATED WITH CAUSTIC POTASH OR SODA.

<i>Acids.</i>	<i>Methyl</i>	<i>Phenolphthalein.</i>		<i>Litmus.</i>	
	<i>Orange.</i> <i>Cold.</i>	<i>Cold.</i>	<i>Boiling.</i>	<i>Cold.</i>	<i>Boiling.</i>
Sulphuric, H_2SO_4	2	2	2	2	2
Hydrochloric, HCl	1	1	1	1	1
Nitric, HNO_3	1	1	1	1	1
Thiosulphuric, $\text{H}_2\text{S}_2\text{O}_3$	2	2	2	2	2
Carbonic, H_2CO_3	0	1(dilute)	0	—	0
Sulphurous, H_2SO_3	1	2	—	—	—
Hydrosulphuric, H_2S	0	1(dilute)	0	—	0
Phosphoric, H_3PO_4	1	2	—	—	—
Arsenic, H_3AsO_4	1	2	—	—	—
Arsenious, HAsO_2	0	—	—	0	0
Nitrous, HNO_2	} Indicator destroyed	1	—	1	—
Silicic, H_4SiO_4		—	—	0	0
Boric, H_3BO_3	0	—	—	—	—
Chromic, H_2CrO_4	1	2	2	—	—
Oxalic, $\text{H}_2\text{C}_2\text{O}_4$	—	2	2	2	2
Acetic, $\text{HC}_2\text{H}_3\text{O}_2$	—	1	—	1(nearly)	—
Butyric, $\text{HC}_4\text{H}_7\text{O}_2$	—	1	—	1(ditto)	—
Succinic, $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$	—	2	—	2(ditto)	—
Lactic, $\text{HC}_3\text{H}_5\text{O}_3$	—	1	—	1	—
Tartaric, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$	—	2	—	2	—
Citric, $\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	—	3	—	—	—

When a blank (—) is left the end reaction is obscure, and not to be depended on.

Some Laboratory Apparatus.—E. Pollak, Rep. anal. Chem. 7, 287, describes a stoppered funnel tube so modified as to deliver a constant supply of liquid. The bulb of the funnel tube is narrowed at the top to a small opening in which is ground a hollow stopper, prolonged into a tube reaching nearly to the stop-cock in the neck of the funnel. The side of this stopper is perforated, and an opening in the neck to correspond is made by melting in a short glass tube. The arrangement works on the principle of a Mariotte's bottle.

A second piece of apparatus described is a wide angle funnel with a short neck for filling tubes, etc. The neck is widest at the point so as to prevent powders from clogging it.

The author also describes a form of condenser which appears to have little to recommend it. The vapor to be condensed passes into a wide tube, inside of which another slightly smaller tube, closed at both ends, is inserted. Through the smaller tube cold water is passed—in at one end and out at the other.

INORGANIC ANALYSIS.

Detection of Traces of Chromium.—Donath and Jeller, Rep. anal. Chem. 7, 33. The solution is treated with sodium carbonate and potassium permanganate, boiled, some alcohol added to reduce the excess of permanganate, and filtered. The filtrate is acidified with HCl, and tested with a little starch paste and fresh potassium iodide solution. If the chromium is to be estimated the process is the same except that the chromium solution is run slowly into the mixed hot solution of carbonate and permanganate from a pipette and the mixture boiled for ten minutes. The filtrate is acidified, heated with a little alcohol and precipitated with ammonium sulphide.

Determination of Copper in Rich Ores.—Donath and Jeller, Rep. anal. Chem. 7, 34. The powdered ore is heated to redness with double its volume of zinc dust in a porcelain crucible. The mass is then treated with dilute sulphuric acid (1—4) in excess which dissolves the zinc and *iron*, leaving all the copper, partly as sulphide, partly as metal, in the residue. The residue is then dissolved and the copper determined volumetrically in the ammoniacal solution with KCN.

Separation of Manganese from Zinc and Nickel.—Donath and Jeller, Rep. anal. Chem. 7, 36. The authors find that if manganese is precipitated by hydrogen dioxide from its ammoniacal solution in presence of zinc and nickel, small quantities of these metals are carried down with it. If the precipitate is dissolved and precipitated again in the same way, the resulting oxide is free from zinc and manganese. In this way from 50 c. c. of a solution containing 0.1335 gms. Mn_2O_4 to which an unknown amount of zinc was added 0.1334 gms. Mn_2O_4 were obtained. An equal volume of the same solution to which nickel sulphate was added gave 0.1341 gms. after two precipitations. If calcium is present this comes down with

the manganese and cannot be separated from it by a second precipitation.

Volumetric Estimation of Sulphites in Presence of Thio-sulphates.—W. Kalmann, Ber. d. deut. Chem. Ges. **20**, 568. The method is founded upon the following reactions :



In the first hydriodic acid is set free, in the second not. The solution whose content in sulphite is to be estimated is placed in a burette and run into a measured volume of iodine solution until the color disappears. Methyl orange is then added and the amount of hydriodic acid set free estimated with $\frac{N}{10}$ sodium hydroxide. The following results were obtained with a mixture of pure sodium sulphite and thiosulphate :

Na_2SO_3		$\text{Na}_2\text{S}_2\text{O}_3$	
<i>Calculated per cent.</i>	<i>Found per cent.</i>	<i>Calculated per cent.</i>	<i>Found per cent.</i>
3.57	3.29	96.43	97.25
28.28	27.96	71.72	72.01
45.24	45.90	54.75	54.76
55.72	55.61	44.28	43.37
88.07	87.16	11.93	11.48

Iodometric Estimation of Zinc and Cadmium Sulphides.—P. von Berg, Zeit. anal. Chem. **26**, 23. When zinc sulphide is brought in contact with iodine in hydrochloric acid solution, the following reaction takes place: $\text{ZnS} + 2\text{HCl} + \text{I}_2 = \text{ZnCl}_2 + 2\text{HI} + \text{S}$. The analysis is conducted as follows: The sulphide of zinc is washed into a stoppered flask, from which the air has been driven by CO_2 ; the flask contains about 800 c. c. water previously boiled. The filter is also thrown in and the contents strongly shaken to divide the zinc sulphide. Concentrated hydrochloric acid and iodine solution in excess are then added, and after shaking again the excess of iodine is measured at once with standard thiosulphate. In this way the author obtained with zinc, 98.96, 100.16, 99.68, 98.99, 99.32, and 99.48 per cent. zinc instead of 100 per cent. and with cadmium 98.81, 99.64, 100.20, 100.10 and 99.22 instead of 100 per cent.

Detection of Sulphite in Presence of Thiosulphates and Sulphates.—A. Villiers, *Compt. Rendus.* 104, 1177. This method depends upon the fact that normal sulphites are alkaline to litmus while acid sulphites are neutral. If to a solution containing a sulphite litmus is added and then dilute hydrochloric acid until the solution turns faintly red, carefully avoiding an excess, and then barium chloride, half of the sulphurous acid precipitates, the rest remains in solution.



If the filtrate from the barium sulphate is boiled the sulphurous acid distills off and can be collected and examined in the usual way.

[Thompson has shown (*Jour. Soc. Chem. Ind.* 6, 195) that methyl orange is a better indicator for sulphurous acid than litmus, and that it behaves in the same way towards it. Probably methyl orange could be substituted for litmus with advantage.—ED.]

Estimation of Alumina in Wine and Grapes.—L. L'Hôte, *Compt. Rendus.* 104, 853. 250 c. c. of the wine is evaporated in a platinum capsule nearly to dryness, sulphuric acid added, the mass carbonized and ignited in a muffle to burn off the carbon. The ash is heated with 15 c. c. nitric acid and from the solution the phosphoric acid is thrown down by 100 c. c. ammonium molybdate solution. From the filtrate the iron and alumina are thrown down together by adding ammonia and ammonium sulphide in excess. The iron is then separated from the alumina by reducing in a current of hydrogen at a red heat and subsequently passing hydrochloric acid gas over it. The silica present in the residue is removed by hydrofluoric and sulphuric acids. The author finds that the amount of alumina in wine varies from 0.000 to 0.036 gms. per liter.

A New Color Reaction for Bismuth.—K. Hasebrock, *Ber. d. deut. chem. Ges.* 20, 213. If to a solution of bismuth, ammonia in excess and then hydrogen peroxide be added, the white precipitate of bismuth hydroxide at first obtained turns yellow from its conversion into bismuthic acid. The author

considers this test a valuable addition to our present method for the detection of bismuth.

The Use of Nitroso Beta Naphtol in Quantative Analysis.—G. V. Knorre, Ber. d. deut. Chem. Ges. 20, 283, has continued the examination of the behavior of this reagent begun by Ilinski and Knorre.*

Copper Nitroso Beta Naphtol.

This is obtained as a coffee-brown precipitate with a metallic luster when a neutral copper salt is added to a solution of nitroso beta naphtol in 50 per cent. acetic acid. This precipitate is soluble in warm, dilute hydrochloric and sulphuric acids and separates out more or less completely, according to the strength of the acid, as the solution cools. The compound is easily soluble in warm, glacial acetic acid and dissolves in considerable amount when the acid is cold. 50 per cent. acetic acid dissolves traces when cold, rather more when warm.

I. SEPARATION OF COPPER FROM LEAD, CADMIUM, MAGNESIUM, MANGANESE, MERCURY, ZINC, ETC.

The metals must be present as chlorides or sulphates. The solution is neutralized with ammonia, acidified slightly with a few drops of hydrochloric acid, evaporated to a small bulk, and while boiling a filtered solution of nitroso beta naphtol in 50 per cent. acetic acid is added. For one part copper contained in the solution, about five parts of the nitroso naphtol should be added. After standing several hours in the cold the precipitate is filtered and carefully washed. As the precipitate contains free nitroso naphtol the wash water will have a yellow color even after the precipitate is completely washed. The dried precipitate is ignited very carefully in a platinum crucible. If large quantities of copper are present it is best to add a little oxalic acid or ammonium oxalate to ensure quiet decomposition of the compound. The copper is weighed as oxide.

* Ber. d. deut. chem. Ges. 18, 699 and 2728.

Test Analyses.

<i>No.</i>	<i>Copper Taken.</i>	<i>Copper Found.</i>
1	0.2133 gms.	0.2132 gms.
2	0.2133 "	0.2128 "
3	0.2133 "	0.2129 "

a.—Taken, 0.2031 gms. copper and 1.7550 gms. cadmium, as sulphates ; found, 0.2029 copper.

b.—Taken, 0.2031 copper and 0.5350 magnesia, as sulphates ; found, 0.2033 copper.

c.—Taken, 0.2031 copper and 0.6079 manganese, as sulphate and chloride ; found, 0.2021 copper.

d.—Taken, 0.2031 copper and 1.2076 zinc oxide, as sulphates ; found, 0.2021 copper.

Brass wire by this method gave 63.04 and 63.07 per cent. copper ; by precipitation as sulphide 63.10 per cent.

e.—Taken, 0.1323 copper, as double chloride of copper and ammonium, and 0.5884 mercuric chloride ; found 0.1327 copper. A second experiment gave 0.1329 copper.

f.—Weighed amounts of copper ammonium chloride and lead acetate were dissolved in water, and acetic acid added to the solution of the first salt, so that on mixing no precipitate of lead chloride formed.

<i>No.</i>	<i>Copper Taken.</i>	<i>Lead Taken.</i>	<i>Copper Found.</i>
1	0.2502	0.2512	0.2499
2	0.2502	0.2512	0.2503
3	0.1401	1.2427	0.1493
4	0.1491	1.2427	0.1490

In the filtrate from the copper the lead may be determined as sulphide. From No. 4, 1.2414 gms. lead were obtained in this way.

If silver is present this is partly precipitated with the copper.

II. SEPARATION OF IRON FROM CHROMIUM, MANGANESE, NICKEL, ZINC, ETC.

Ilinski and Knorre* have shown that iron may be separated from aluminum by means of nitroso beta naphthol ; it is easy also to separate it from the above metals by the same operation.

*Ber. d. deut. Chem. Ges. 18, 2728.

The method is the same as for copper. The iron should be present as ferric chloride or sulphate. The presence of small amounts of ferrous salts does not interfere with the accuracy of the method. For 0.1 gm. iron present at least 1 gm. nitroso naphthol should be added. Not more than 0.3 gms. iron should be taken, as otherwise the precipitate obtained is too bulky.

Separation of Iron and Manganese.

To separate the manganese in the filtrate from the iron the author uses the method of Wolff.* The evaporated filtrate is poured into an Erlenmeyer's flask, ammonium chloride and ammonia in large excess added and the manganese precipitated by passing a current of air saturated with bromine vapor through the solution. The precipitation is complete in fifteen to twenty minutes. The following results were obtained :

<i>No.</i>	<i>Iron taken gms.</i>	<i>Mn taken gms.</i>	<i>Iron found gms.</i>	<i>Mn found gms.</i>
1	0.1806	0.0476	0.1802	_____
2	0.1058	0.1584	0.1052	_____
3	0.2013	0.6079	0.2023	_____
4	0.2018	0.6079	0.2019	_____
5	0.1009	0.3541	0.1013	_____
6	0.1009	0.3541	0.1006	_____
7	0.1190	0.0639	0.1192	0.0635
8	0.1190	0.0639	0.1193	0.0633
9	0.1190	0.0639	_____	0.0640
10	0.1190	0.0639	0.1193	0.0635
11	0.1190	0.0639	_____	0.0640
12	0.0982	0.0639	0.0982	0.0635
13	0.0982	0.0639	0.0980	0.0635

Separation of Iron from Zinc.

1.—Taken, 0.1395 gms. ferric oxide, as ferric ammonium sulphate, and 0.5210 gms. zinc sulphate ; found 0.1398 ferric oxide.

2.—Taken, 0.1806 gms. iron, as ferric ammonium sulphate, and 0.4308 gms. zinc sulphate ; found 0.1806 gms. iron.

3.—Taken, 0.2018 gms. iron, as ferric chloride, and 1.2076 zinc oxide, as sulphate ; found 0.2023 iron and 1.2081 zinc oxide (precipitated as carbonate from the filtrate).

*Zeit. anal. Chem. 22, 550.

Separation of Iron from Nickel.

This separation offers no difficulty. The nickel is precipitated as hydrated sesquioxide by adding caustic potash and bromine water to the filtrate from the iron. A piece of nickel plated sheet iron which contained 87.15 per cent. iron gave

	I	II
Iron	87.05	87.15
Nickel	12.70	12.81
	<hr/> 99.84	<hr/> 99.96

Separation of Iron from Chromium.

If iron is precipitated from a solution containing chromium by the above method the results obtained are too high, part of the chromium being precipitated with the iron. In presence of chromium therefore it is necessary to add about 5 c. c. hydrochloric acid, sp. gr. 1.12 before adding the nitroso naphthol. This prevents the precipitation of chromium and does not interfere with the complete separation of the iron. In the filtrate from the iron the chromium cannot be completely thrown down with ammonia, and it is necessary to first determine iron plus chromium with ammonia, then iron with nitroso naphthol and estimate the chromium by difference.

1.—Taken, 0.1403 gms. Fe_2O_3 as ferric ammonium sulphate and 0.1420 gms. Cr_2O_3 as chrome alum ; found, 0.1404 gms. Fe_2O_3 .

2.—Like 1. Found 0.1406 Fe_2O_3 .

3.—Taken, 0.1505 gms Fe_2O_3 and 0.2620 gms. Cr_2O_3 ; found 0.1503 Fe_2O_3 .

Estimation of Phosphoric Acid in Presence of Alkaline Salts.—A. Villiers, Comptes Rendus. 104, 1103. Bull. soc. Chem. 47, 547, finds that, for reasons given in his paper, phosphoric acid cannot be estimated in presence of alkaline salts by means of baryta water ; neither can acids be estimated by baryta water in presence of sodium phosphate. Both of these determinations can be made, under the conditions given, when caustic potash or soda is used as the reagent.

On Weil's Method for Sulphur in Sulphides.—C. Friedheim, Ber. d. deut. chem. Ges. **20**, 59, finds Weil's method for the estimation of sulphides (Comptes Rendus, **102**, 1487) a worthless one. First, because in ammoniacal solution copper sulphide carries down copper oxide. Second, because copper sulphide oxidizes in contact with cupric chloride, forming cuprous chloride and sulphuric acid.

Weil states (Ibid **20**, 695) that he now uses a Fehling's solution, containing 39.3375 gms. copper sulphate, 197 gms. Rochelle salt, and 125 gms. sodium hydroxide per liter for absorbing the sulphuretted hydrogen. By using this solution he obtains accurate results. With an antimony glance containing 28.15 per cent. sulphur, he obtained by this method 28.38, 28.18 and 28.59 per cent.

To this Friedheim replies that he has used the modified method and failed in obtaining correct results. Instead of 28.59 per cent. sulphur in antimony glance he obtained 29.29, 32.65, 32.11, 31.45 and 30.42 per cent., the results, except in the first case, being too high. The high results are caused by the formation of oxysulphide of copper.

The Determination of Vanadic Acid.—M. A. Ditte, Comptes Rendus, **104**, 982. When ammonium vanadate mixed with ammonium chloride, as obtained in Berzelius' method, is ignited vanadic acid volatilizes. In order to get rid of the ammonium chloride and so obviate loss by volatilization the author proceeds as follows: If the liquid is acid, ammonia is added, the liquid being at the same time heated, until it becomes colorless. The solution is now cooled to 30° to 40° and crystals of NH_4Cl added to nearly saturate the solution and precipitate the vanadate and then 4 or 5 volumes of alcohol are added. This mixture is then allowed to stand for several hours and finally filtered and washed with alcohol in which the vanadate is insoluble. Any ammonium chloride which precipitates when the alcohol is added redissolves as the washing proceeds. If the solution contains alkalies it is first precipitated with ammonium chloride, washed with a solution of the same substance and the precipitate redissolved in hot water

and treated as above. [According to Roscoe, (see Roscoe and Schorlemmer's Treatise, Vol. II, Pt. II, Page 299) Berzelius' method is inferior in accuracy to the one founded upon the precipitation of the vanadic acid as lead vanadate.—Ed.]

IRON AND STEEL.

EDITED BY P. W. SHIMER.

On the Action of Nitrogen on Iron.—H. N. Warren, Research Analyst, Chem. News, 55, 155. Pure dry ammonia gas was passed over pieces of finest merchant iron varying in thickness from $\frac{1}{4}$ of an inch to 6 inches, and kept at a bright red heat for from 2 to 12 hours. The iron took up from 0.004 to 0.5 per cent. nitrogen, and became white, highly crystalline and brittle. Iron containing 0.5 per cent. nitrogen broke transversely when allowed to fall from a height of 6 feet.

On substituting anhydrous protochloride of iron in place of the iron bar, volumes of ammonium chloride were at once evolved, and a silvery, spongy mass of nitride of iron remained, containing upwards of 4 per cent. of nitrogen.

Determination of Phosphorus in Iron and Steel.—Leop. Schneider, Oesterr. Zeitschrift für Berg-und Hüttenwesen, 47, 765. It is well known that the determination of phosphorus by solution in nitric acid and precipitation by ammonium molybdate gives low results when the solution has not been evaporated to complete dryness. Eggertz supposes this to be due to the formation of a modification of phosphoric acid not precipitable by ammonium molybdate. Tamm and others believe that the carbonaceous matter formed by the action of the nitric acid upon combined carbon prevents the complete precipitation of phosphorus by molybdate. The author however shows that when iron is simply dissolved in nitric acid, the

phosphorus does not go into solution completely as phosphoric acid, but that a part dissolves as phosphorous acid. If potassium permanganate solution is added to the molybdate filtrate the phosphorous acid is oxidized and a further precipitation of phospho molybdate takes place. When, however, the nitric acid solution is evaporated to hard dryness, the phosphorous acid is completely oxidized.

The Chemical Combination of Phosphorus in Pig Iron.—Leop. Schneider, *Oesterreichische Zeitschrift für Berg-und Hüttenwesen*, **45**, 735. Various kinds of iron (spiegeleisen, white and gray pig iron) were shaken up with a solution of cupric chloride until the precipitated copper was redissolved. The residue was boiled for an hour with the same solution and then washed successively with water, boiling caustic potash solution, alcohol and ether, and finally heated in a stream of hydrogen. The metallic powder thus obtained, when separated from admixed carbon by means of a magnet, was found to be crystalline, but did not show distinct crystal forms. In dilute hydrochloric acid it was almost insoluble, but was readily soluble in nitric acid and aqua regia. In concentrated hydrochloric acid it dissolved slowly with evolution of phosphoretted hydrogen.

The substance thus obtained was found to be a compound of phosphorus and iron in proportions corresponding to the formula Fe_3P . This compound has been produced synthetically and described by Hooslef (*Journal für prakt. Chemie* LXX, 149) and Percy (*Percy-Wedding Eisenhüttenkunde*, II. Band, I. Abthlg.)

The percentage of phosphorus in the phosphide was found to rise rapidly with the manganese. When the amount of phosphorus corresponding to all the iron was taken from the total phosphorus, that which remained was enough to combine with all the manganese as Mn_3P_2 . The following are the analyses of the irons experimented on and of the residues of phosphide obtained from them, the latter being calculated to 100 parts of iron :

Composition of Pig Iron.

Composition
of the Residue.

Comb. C.	Gra- phite	P	Si	Mn	S	Cu	P	Mn
3.3	—	2.5	0.06	0.2	0.04	—	18.6	—
—	—	1.45	—	—	—	—	18.6	—
3.56	—	0.53	0.07	2.47	0.028	0.03	18.2	—
—	2.2	1.48	4.0	Tr.	Tr.	Tr.	18.2	—
0.55	2.85	0.94	1.8	0.07	0.01	0.01	18.5	—
—	—	2.01	0.46	4.33	Tr.	Tr.	20.5	5.7
3.98	—	3.4	0.89	18.15	—	—	37.7	52.8
5.28	—	0.38	Tr.	28.7	Tr.	Tr.	38.8	54.4

Manganese in Steel and Iron.—H. C. Babbitt, Am. Chem. Journal, 9, 58. The author was led to try red lead, Pb₂O₄, instead of lead peroxide for the oxidation of manganese to permanganic acid, and obtained the following results on a sample of steel containing .515 per cent. manganese, determined by the acetate of soda and bromine process :

A		B	
No. 1516	.512	per cent. manganese.
" 2516	.513	" "
" 3513	.518	" "
" 4518	.518	" "
" 5513	.518	" "
" 6513	.513	" "

The method of procedure was as follows : .5 gram steel was dissolved in 15 c. c. HNO₃ (1.15 to 1.20 sp. gr.), in a 50 c. c. beaker. The solution was boiled till nitrous fumes ceased, red lead added—in A, one gram ; in B, two grams. The solution was then diluted to about 30 c. c. with hot water. In No. 1 the solution was simply stirred after its addition ; in No. 2, heated to boiling ; No. 3, boiled for one minute ; No. 4, for two and a half minutes ; No. 5, five minutes ; No. 6, fifteen minutes. The solutions were then set aside to allow the residual lead peroxide to settle, the supernatant liquid decanted and the residue boiled with more hot water containing from 20 to 25 per cent. nitric acid. These decantations are continued as long as they show a decided color of permanganic acid. When the manganese is below .60 per cent., one de-

cantation and subsequent boiling is generally sufficient. The combined decantations are then filtered through asbestos and titrated with a standard reducing agent.

Determination of Vanadium in Rocks and Ores.—M. L. L'Hôte, *Comptes Rendus* (CIV., p. 990). *Chem. News*, 55, 191. In a former memoir (*Comptes Rendus*, Dec. 7th, 1885) the author has given a process for extracting from vanadylite the totality of its vanadium in the state of vanadyl chloride, by utilizing the different volatility of the chlorides at a given temperature. This process may be applied to the determination of vanadium in rocks and ores.

The method comprises two operations : the extraction of the vanadium as a vanadic solution, and its volumetric or gravimetric determination.

To isolate the vanadium, dry chlorine is passed over an intimate mixture of four parts of the sample and one part of charcoal, contained in a tube heated to 250° in a special furnace. In case of ores which are almost always arseniferous, the mixture must be previously made into a paste with oil, and calcined at a red heat. When operating upon rocks this precaution is needless. Schloësing's apparatus is used for generating chlorine.

The tube containing the mixture is connected to a system of condensers formed of two Mohr's bulb-tubes. As vanadyl chloride in presence of water forms vanadic acid, the presence of vanadium is indicated by the formation of a red coating in that part of the first tube connected directly with the apparatus.

If there is only a very little vanadium in the rock examined, the liquid of the first bulb is not colored. The vanadium may be detected by dissolving the condensed product in weak hydrochloric acid. The solution on evaporation gives a residue which, if moistened with a drop of colorless ammonium sulphide, takes the purple color characteristic of vanadium sulphide.

The vanadium is determined by following Margueritte's method applied to the determination of small quantities of

iron. We first prepare a standard solution of vanadic acid by dissolving pure vanadic acid in sulphuric acid ; 10 c. c. of this liquid represent 0.0028 gram. of vanadium. Numerous experiments have proved that vanadium may be determined, like iron, by reducing the vanadic salt with zinc.

The solution of permanganate used is $\frac{1}{1000}$. With such a dilution it is necessary to use certain precautions in order to seize the end of the reaction. The liquids must be hot, and distilled water must be used having no action upon permanganate. Common distilled water always decolorizes dilute solutions of permanganate. It is obtained sufficiently pure by redistilling it over permanganate crystals and preserving it from atmospheric dust.

When the quantity of vanadic acid is high, as in certain ores, the liquid in the first bulb turns a greenish blue. The acid solution, mixed with ammonia and evaporated to dryness, gives a residue which, if heated to redness, may be weighed as vanadic acid.

Decomposition of Chrome Iron Ore.—Ed. Donath, Dingler's Polytechnisches Journal, 263, 245. The author finds in barium dioxide a powerful oxidizing and decomposing agent by means of which chrome iron ore may be completely decomposed in a porcelain crucible by aid of an ordinary Bunsen burner. For this purpose the chrome iron ore must be very finely ground, as also the mixture of chrome iron ore with 5 parts of barium dioxide. After heating the mixture $\frac{1}{2}$ hour in a porcelain crucible over a Bunsen burner a greenish-yellow, strongly sintered mass is obtained, which dissolves completely after some hours in water acidulated with hydrochloric acid, and contains in the yellowish-red solution all the chromium as chromic acid.

From this solution the barium is precipitated by means of the least possible excess of sulphuric acid, the filtrate from the barium sulphate is completely neutralized with sodium carbonate and poured into a solution of potassium permanganate to which sodium carbonate has been added. The metallic oxides are precipitated along with sesquioxide of chromium

which is immediately converted into soluble chromate. The excess of permanganate is decomposed by addition of a few drops of ferrous sulphate to the hot solution, and the alkaline chromate solution is filtered off. In this the chromic acid is determined volumetrically by means of a standard iron solution.

MINERAL ANALYSIS.

EDITED BY JOHN EYERMAN.

Gadolinite from Colorado.—L. G. Eakins, (Proc. Colo. Sci. Soc. II, Part I, 32) describes and gives analyses of Gadolinite from Devil's Head, Douglas Co., Col.

	I	II
Sp. gr. at 25° C	4.56	4.59
SiO ₂	22.13* ₁	21.86
Al ₂ O ₃	2.34	0.54
Fe ₂ O ₃	1.13	3.59
ThO ₂	0.89* ₂	0.81
Ce ₂ O ₃	11.10* ₃	6.87
(La Di) ₂ O ₃	21.23	19.10* ₅
Er ₂ O ₃	12.74* ₄	15.80* ₆
Y ₂ O ₃	9.50* ₄	12.63* ₆
FeO	10.43	11.36
BeO	7.19	5.46
MnO	—	0.11
CaO	0.34	0.47
MgO	0.14	0.16
K ₂ O	0.18	0.20
Na ₂ O	0.28	0.32
H ₂ O	0.86	0.74
	100.	100.02

I. Specimen resembled a water-worn stone; when broken, a black, slightly lustrous surface was exposed.

II. Color less dark than I approaching at places to a dull green.

*₁ Mean of 22.10 and 22.15.

*₂ *₃ A second determination gave for ThO₂+Ce₂O₃=11.82.

*₄ The molecular weight of the mixed oxides Er₂O₃ and Y₂O₃=296.

*₅ Didymium absorption line very strong.

*₆ The molecular weight of the mixed Er₂O₃ and Y₂O₃=294.

Allanite from near Statesville, N. C.—An analysis of this mineral by H. F. Keller (Genth's Cont. to Min.) resulted :

SiO ₂	31.685	FeO	10.110
Al ₂ O ₃	17.330	MnO	1.025
Fe ₂ O ₃	7.052	CaO	10.785
Ce ₂ O ₃	18.990*	MgO	0.540
Di ₂ O ₃		Na ₂ O	0.210
La ₂ O ₃		K ₂ O	tr.
Y ₂ O ₃	1.120	H ₂ O	1.460
Er ₂ O ₃		Total	100.307

Meteorite from Arkansas.—G. F. Kunz (Amer. Jour. Sci. June 1887, p. 494) gives a description of a meteorite which fell near Cabin Creek, Johnson Co., Ark., March 27, 1886. An analysis by J. E. Whitfield (Amer. Jour. Sci., June, 1887, p. 500) resulted :

Sp. gr.	7.837
Fe	91.87
Ni	6.60
Co	trace
S	0.05
Comb. C	0.15
P	0.41
Mn	trace
Cl	trace
Insol. in HCl	0.34
	<hr/>
	99.42

Meteorite from Kentucky.—J. E. Whitfield (Amer. Jour. Sci., June 1887) gives an analysis of a meteorite from near Scottsville, Allen Co., Ky. :

Sp. gr.	7.848
Fe	94.37
Ni	5.01
Co	trace
S	0.34
P	0.16
Total C	0.12
	<hr/>
	99.95

* Of which about 5 per cent Ce₂O₃, balance mostly Di₂O₃.

Vanadinite from Arizona.—F. A. Genth (Cont. to Min.) gives analyses of vanadinite from Mammoth Gold Mine, near Oracle, Pinal Co., Ariz.

Color, yellow to orange yellow, orange red, aurora red to brownish red, often variegated.

	<i>Brownish.</i>	<i>Bright Orange Red.</i>
Sp. gr.	6.572	—
Cl	2.41	2.46
Fe ₂ O ₃	0.48	—
CuO	—	—
PbO	77.49	77.47
V ₂ O ₅	16.98	17.16
As ₂ O ₃	3.06	4.30
P ₂ O ₅	0.29	tr.
	—	—
	100.71	101.39
less O, equiv. to Cl=	0.55	0.56
	—	—
	100.16	100.83

Analyses by H. F. Keller.

An analysis by Genth of a brownish olive green vanadinite from Yavapai Co., Arizona resulted :

Sp. gr.	7.109
Cl	2.69
Fe ₂ O ₃	0.04
CuO	0.18
PbO	77.96
V ₂ O ₅	18.64
As ₂ O ₃	tr.
P ₂ O ₅	0.72
	100.23
less O, equiv. to Cl=	0.61
	—
	99.62

Brochantite from Chili.—A. H. Chester (Amer. Jour. Sci. April, 1887, pp. 287.) gives an analysis of brochantite from Chili. The mineral is associated with linarite.

CuO	71.73
SO ₃	18.21
H ₂ O	10.06

Hessite from Arizona.—F. A. Genth in his contributions to Mineralogy, No. 29, (Proc. Amer. Phil. Soc. 18th March, 1887) gives an analysis of Hessite from West Side mine, Tombstone, Cochise Co., Arizona.

Ag	62.87	62.34
Pb	0.28	0.30
Te	37.34	37.05
Se	tr.	tr.
	<hr/>	<hr/>
	100.49	99.69

Emmonsite, a Ferric-Tellurite from Arizona.—W. F. Hillebrand (Proc. Colo. Sci. Soc. II, Part I, 20,) gives a description and analyses of a ferric-tellurite, which he has named Emmonsite, from near Tombstone, Arizona. Color yellowish green, translucent and occurring in crystalline scales and patches throughout a rather hard and brownish gangue. System probably monoclinic. Sp. gr. about 5.

	I	II	III	IV	mean
Te(Se)	59.77	59.15	59.05	59.14	58.75
Fe	14.00	14.06	14.90	14.20	14.29
ZnO				1.94	Se 0.53
CaO				0.56	
H ₂ O	3.28				unknown

The Te, Se and Fe of analyses IV require 20.94 per cent. oxygen on the assumption of the ferric-tellurite composition, making a total of 96.78, leaving 3.22 per cent. for H₂O, and possible SO₃ and SiO₂ (for gypsum and calamine if present).

Meteorite from Albuquerque, New Mexico.—L. G. Eakins (Proc. Colo. Sci. Soc. II. Part I. 14) has analysed a meteorite from New Mexico with the following results :

Fe	Ni	Co	Cu	Zn	Mn	P	S	Si	Total
88.760	9.860	.510	.034	.030	tr.	.182	.012	.044	99.432

which represents the following constitution :

Nickeliferous iron	98.224
Troilite (FeS)	.033
Schreibersite (Ni ₃ Fe ₄ P)	1.175
	<hr/>
	99.432

ATOMIC WEIGHTS.

EDITED BY F. W. CLARKE.

Silicon.—Thorpe and Young (Jour. Chem. Soc., June, 1887) have redetermined the atomic weight of this element by means of the bromide. The latter, carefully purified, was decomposed by water, and then evaporated to dryness in a tarred porcelain crucible. The residual silica was weighed.

9.63007	gm.	SiBr ₄	gave	1.67070	gm.	SiO ₂ .
12.36099	"	"	"	2.14318	"	"
12.98336	"	"	"	2.25244	"	"
9.02269	"	"	"	1.56542	"	"
15.38426	"	"	"	2.66518	"	"
9.74550	"	"	"	1.69020	"	"
6.19159	"	"	"	1.07536	"	"
9.51204	"	"	"	1.65065	"	"
10.69317	"	"	"	1.85555	"	"

The foregoing figures represent vacuum weights, and give, with Meyer and Seubert's values for O, H, and Br, values for the atomic weight of silicon ranging from 28.243 to 28.429, in mean, 28.332. So great a range of variation for so low an atomic weight is hardly satisfactory; and further data are needed.

Gold.—Thorpe and Laurie (Jour. Chem. Soc., June, 1887,) have determined the atomic weight of gold by means of potassium auribromide, KAuBr₄; the salt which was previously used by Krüss. Three sets of ratios were made use of.

1st. The auribromide was decomposed by ignition, and the ratio between the residual Au and KBr was ascertained.

2d. The potassium bromide from the previous series of experiments was titrated with a standard solution of silver, giving the ration Au : Ag.

3d. The silver bromide found in the second series was weighed, giving the ratio Au : AgBr. The results, using Stas' values for K, Ag, and Br, and putting H=1, were as follows :

1st series, Au : KBr, eight experiments, Au=196.876.

2d " Au : Ag, nine " " =196.837.

3d " Au : AgBr, eight " " =196.842.

Mean, twenty-five experiments, " =196.852.

Zinc.—Reynolds and Ramsay (Chem. News, 55, 269,) have estimated the amount of hydrogen evolved upon the solution of pure zinc in an acid. Twenty-nine experiments were made, and five, which are fully corrected, give the following values for Zn :

65.5060

65.4766

65.4450

65.5522

65.4141

Mean, 65.4787 \pm .016135.

The weight of hydrogen was determined from its volume by means of Regnault's data.

Thorium.—Krüss and Wilson (Ber. 20, 1665) have reinvestigated both the equivalent and the atomic weight of thorium. The density of the chloride at 1057°, is 12.424; the theoretical value for ThCl₄ being 12.928. The atomic weight is deduced from eight analyses of the sulphate Th(SO₄)₂. Using absolute weights the value ranges from Th=231.813 to Th=231.916. In mean, Th=231.869, when O=15.96 and S=31.98.

ORGANIC ANALYSIS.

The Analysis of Sugar-Cane and Beet Juice.—C. A. Crampton (Chem. News 55, 207) gives the mode of procedure used by the Chemical Division of the U. S. Dept. of Agriculture in the experiments of the department on sorghum and sugar-cane, together with a table for the rapid calculation of analyses. The method of manipulation is designed to secure a reasona-

ble degree of accuracy and at the same time be as rapid as possible. Instead of taking 100 c. c. of the juice in a flask graduated to 100 and 110 c. c., adding 10 c. c. of lead solution, filtering and polarizing, as is the custom in the beet sugar houses in France and Germany, 50 c. c. only are taken, lead added, and the volume brought to 100 c. c., filtration being greatly facilitated in this way.

The detailed procedure is as follows :

Fifty cubic centimeters of the juice is measured out by means of an accurately calibrated pipette and run into a 100 c. c. flask ; to it is added from 1 to 4 c. c. of a strong solution of sub-acetate of lead, the whole made up to the mark with water, filtered, and polarized.

The same solution is then used for the determination of the reducing sugars by Fehling's solution, the excess of lead being precipitated by sulphate of soda. As the reduction of copper sub-oxide by sugars has been shown to be affected by the amount of dilution in which the action takes place, it is desirable to have as nearly as possible a constant amount of dilution, and the most favorable dilution is such that from 10 to 20 c. c. of the solution will be required to reduce the copper from 10 c. c. of Fehling's solution ; so, for juice presumed to contain from 1 to 2 per cent. of reducing sugars, 50 c. c. of the solution, which has been polarized, made up to 100 c. c. will furnish the proper dilution ; for those containing from 2 to 3 per cent., 50 to 150 c. c., and so on. In the case of juices containing less than 1 per cent. of reducing sugars the excess of lead may be removed by adding the sodic sulphate before the lead precipitate is filtered off, when the same solution can be used for polarization and for the reducing-sugar determination. The copper solution used is Violette's modification, and the operation is performed in large test-tubes from 9 to 10 inches long and of about 1 to 1½ inch caliber, and the end reaction is obtained with ferrocyanide of potash and acetic acid, the small portion of clear liquid required being filtered out by means of Wiley's tubes (*Bull. de l'assoc. des Chim. de Sucr. et de Dist.*, April, 1884). These

tubes are simply glass tubes about nine to ten inches long and one-fourth inch caliber. At one extremity a slight rim is made by turning back the edge while hot, and over this is stretched and tied a piece of fine linen cloth. To use the tube it is inserted into a beaker of water containing in suspension a quantity of very finely ground asbestos ; by suction at the other end of the tube the linen cap is covered with a film of asbestos and it is then immediately inserted into the test-tube containing the hot precipitated Fehling solution ; suction is again made on the tube and the portion of clear liquid obtained is run into a porcelain dish containing the test solution by simply inverting the tube. These tubes may be cleaned and used over and over again by washing off the asbestos film, dissolving out any sub-oxide of copper which may remain in the cloth by soaking in nitric acid and rinsing in water until they no longer taste acid. One covering of linen suffices for many tests, and when worn out it is easily replaced.

The author says : "Working in this way a large number of samples can be analyzed in a day, twenty-five to thirty being generally a fair day's work for operators on the stations of the Department of Agriculture, both sucrose and glucose being determined, and also the total solids (from the specific gravity), and this number is much exceeded in case of stress of work by allowing the polarizations to stand until night, using all the daylight for glucose determinations. By having a boy measure out the samples and prepare them for analysis the amount of work done can be nearly doubled."

The table given contains degrees Brix. and the corresponding specific gravity, and opposite to these factors for the calculation of sucrose and glucose in juices of the corresponding specific gravities, when the mode of procedure given above has been followed. Two factors for sucrose are given, one for instruments using as a normal quantity 26.048 gms. of sugar, such as the Soleil-Scheibler, and one for those using 16.3 gms., such as the Laurent.

This paper has also been published as part of Bulletin No. 15 of the Division of Chemistry, U. S. Dept. of Agriculture.

Analysis of Gun Cotton.—G. Lunge, Ding. poly. Jour. 262, 224. The gun cotton is placed in the beaker of the nitrometer which is closed by means of a cork and bent funnel tube as shown in the figure. 2–3 c. c. concentrated sulphuric acid is then poured on the gun cotton and when this is completely dissolved the estimation is finished in the usual way. The escape of nitrous fumes during the solution of the gun cotton is entirely prevented by this slight modification and accurate results are obtained. This arrangement can also be used for dynamite and other explosives of this class. The following results were obtained :

No.	Gun Cotton Taken.	Volume of Gas Found.	Barometer.	Thermometer.	Per cent. Nitrogen.
I	0.5252 gms.	113.1 c. c.	725 mm.	17°	12.07
II	0.5159 "	111.3 "	725 "	18°	12.07
III	0.5120 "	110.3 "	725 "	18°	12.05

In an appendix Lunge states that Alberts has conducted the analysis of gun cotton in his nitrometer for two years as follows : The sample is first dried for two hours at 40°, then rubbed through a fine brass sieve, about 10 gms. of this dried in the dessicator over sulph. acid until there is no further loss of weight. About .48 gms. is now weighed out in a stoppered flask, 5 c. c. concentrated sulphuric acid added, the mixture stirred with a platinum wire and transferred, without loss of time, to the nitrometer. Any adhering particles are rinsed into the nitrometer with more of the acid, 3 c. c. at a time. The total quantity of acid needed is 15–20 c. c. The analysis is finished in the ordinary way.

Mode of Distinguishing Horseflesh from Beef.—James Bell, Chem. News, 55, 15. The specific gravity of the fat of the horse is 908.4 at 100° F. while beef fat which melts at 110°–116° F. has a calculated sp. gr. at the same temperature of 903.6 to 904. There is further a great difference in the melting point, horse fat melting at 70° F.

Mutton fat differs from horse fat even more than beef fat does.

The fat of horseflesh, like that of beef and mutton, is free from any of the soluble fatty acids.

Estimation of the Fatty Acids in Soap.—R. Bauer, Jour. prak. Chemie, **35**, 88. For weighing the fatty acid obtained from soap by dissolving in light petroleum ether or benzine the author uses an arrangement consisting of two watch glasses. One of these is larger than the other and contains some fragments of broken glass. Upon these fragments the second watch glass is placed. The whole apparatus is now weighed, the solution poured into the inner watch glass and, after evaporating, is weighed again. In this way if any of the acid should creep over the edge of the inner watch glass it is caught by the broken glass.

New Reactions for Resorcinol and the Recently Discovered Coal Tar Febrifuges and Antipyretics.—W. Smith, Jour. Soc. Chem. Ind. **5**, 580.

Test for Resorcinol (Resorcine).—If to a dilute, freshly prepared, aqueous solution of the so-called beta naphthaquinone, a few drops of a one per cent. solution of resorcinol are added, and then a few drops of ammonia, the sample at once assumes a beautiful dark bluish-green color. If a portion of the solution is shaken with ether, little or none of the color is taken up by the ether. If to the bulk of the green fluid nitric acid is added to acid reaction, the green color gives place to a fine red, and ether shaken with this solution takes up the red and becomes finely tinted, the lower layer proportionately losing color, and at length becoming pale yellow or colorless. Chloroform answers as well as ether; the layer, in this case, sinking to the bottom of the vessel. The reaction is specially beautiful if the ethereal solution of *beta naphthaquinone* be used.

Thalline Sulphate or Tartrate.—If to the dilute solution of the *beta naphthaquinone* a small quantity of a solution of thalline sulphate or tartrate be added, and then a drop or two of caustic soda solution, a fine red or cherry-red color is produced, the beauty of which is heightened by acidifying with nitric acid. By shaking the sample with chloroform or ether,

they take up the color and become themselves finely tinted.

To Distinguish a Resorcinol "Salol" from a Phenol "Salol."

—Fuse some of the sample with a little pure potassium or sodium hydroxide in a small silver dish, or boil for some time with a little concentrated alcoholic potassa, when the ether is decomposed, and the resorcinol or phenol remains combined with the potassa. Dissolve in water and pass carbon dioxide in excess to decompose the phenol or resorcinol alkaline compounds, and shake with ether. The ethereal solution will contain the phenol or resorcinol, and now the foregoing test may be usefully applied, when phenol, if present, will give no reaction, only resorcinol giving the beautiful reaction characteristic of it.

Kairine (Hydrochloride of Hydroxy-hydroethyl-quinoline).

—(1) One drop of ferric chloride produces in a dilute aqueous solution a violet coloration, which almost at once changes to brown. Excess of ferric chloride gives a dark brown coloration, and in concentrated solutions a brown-black precipitate. (2) Potassium dichromate when added to a neutral aqueous solution forms a dark coloration at first; after a few seconds or minutes, according to circumstances, a violet coloring matter separates, dissolving in alcohol to a mauve-colored solution.

Antipyrin (Methyl-pyrazol) $C_{10}H_{10}N_2O$, behaves quite differently from the foregoing. It is distinguished: (1) by the red coloration produced on addition of ferric chloride. One part in 100,000 can be detected by this reaction. (2) by the pure blue-green coloration produced by nitrous acid in dilute solutions. The color develops fully after a few seconds. In concentrated solutions green crystals separate. One part in 10,000 can be detected by this test.

Antifebrine (acetanilide $C_6H_5.NH(CO.CH_3)$) gives no color reactions with the foregoing reagents. A small quantity of the substance should be boiled with alcoholic potassa, when the following decomposition will take place:— $C_6H_5.NH(CO.CH_3) + KOH = C_6H_5.NH_2 + CH_3.COOK$. The aniline is easily tested in the usual way, and after distilling it off the residue contains potassium acetate, also readily identified.

Estimation of Cocaine in Coca Leaves.—E. R. Squibb, *Ephemeris*, 3, 912. "The coca leaves are ground into coarse powder, twenty or thirty meshes to the inch. Of this powder 100 gms. is moistened with 100 c. c. of water, containing five per cent. of sulphuric acid, and is packed moderately in a cylindrical percolator, and percolated to 500 c. c. with the same acid water menstruum. This percolation is best done by means of a Sprengel water pump into a flask marked at about 500 c. c., and this amount of percolate will generally exhaust the coca sufficiently even when the leaves are of the thick Bolivian variety. A portion of the stock of the acid water used is then balanced against a portion of the stock of recrystallized carbonate of sodium, and it will generally be found that 6 to 6.5 gms. of the crystals are required to saturate 100 c. c. of the acid water. The percolate is then measured off into a large beaker or other similar vessel, and 50 c. c. of kerosene added to it, and the whole well stirred together. Then as much of the crystallized carbonate of sodium is added as would saturate the percolate if it was all acid water, the sodium salt being added little by little with constant vigorous stirring. In order to precipitate the alkaloid completely, the sodium salt is required in considerable excess, and the difference in acidity between the percolate with its large percentage of extract and the acid water, gives about the proper excess. The kerosene is very thoroughly and repeatedly stirred into the mixture during four or five hours of digestion, and is then separated by means of a separating funnel or small siphon. Then 25 c. c. of fresh kerosene is added to the percolate and the stirring, digestion and separation are repeated twice, making three washings with the kerosene. If an emulsion should form between the percolate and the kerosene it will lie next above the percolate in drawing this off, and should be drawn off into a separate vessel with the final washing. A little dry filter paper pulp, or a little asbestos, or sand stirred into this emulsion will break it up so that the kerosene can be separated completely, when it is added to the larger portion. If the percolate and the kerosene be shaken together, instead of being stirred as above di-

rected, all or nearly all of the kerosene will be made into an emulsion. On standing two or three days this emulsion will separate wholly or partially, but as the operator can never tell beforehand whether it will separate completely or only in part, it is better not to wait, but rather to separate it as directed. Then by stirring rather than shaking, the amount of emulsion is reduced to a minimum, and if the stirring be well done, the percolate is washed free from alkaloid, and this latter is practically all held dissolved in the kerosene. But if the operator wants to be assured that he has washed out all the alkaloid from the percolate, let him add to the latter about two gms. more of carbonate of sodium and 25 c. c. of ether and again stir, or shake and separate. The residue left on the evaporation of this ether should give no cocaine impression on the tongue, nor any saturating power to a very minute quantity of very dilute acid. The 100 c. c. of kerosene holding the alkaloid in solution, is then shaken vigorously in a separator, (see Ephemeris, p. 786) three times,—twice with 10 c. c. of the acid water, and the third time with 5 c. c. of water. This washes out practically all the alkaloid as sulphate, and leaves the kerosene ready for another assay. To the 25 c. c. of solution of sulphate of cocaine contained in another separator 10 c. c. of strong ether is added, well shaken, and then a moderate excess of crystals of carbonate of sodium. After the effervescence this is well shaken and the ether separated. The solution is again washed twice with 10 c. c. more of ether each time. All the ether is then collected, entirely free from even a fraction of a drop of the solution, in a beaker at least three times the capacity of the ether. From this the ether is evaporated and the alkaloid is left in the condition of a light amber-colored varnish on the bottom and sides. If a capsule be used instead of a beaker, or if too small a beaker be used, the ethereal solution is liable to creep over the edges and be lost. As soon as the beaker is free from the odor of ether it may be weighed, and the tare subtracted will give the weight of cocaine obtained from the 100 gms. coca." The highest amount found by the author is .892 per cent.

Examination of Butter Colors.—H. B. Cornwall, Chem. News 55, 49. “About 5 gms. of the warm filtered fat are dissolved in about 50 c. c. of ordinary ether in a wide tube, and the solution is vigorously shaken for ten to fifteen seconds with 12 to 15 c. c. of a very dilute solution of caustic potash or soda in water, only alkaline enough to give a distinct reaction with turmeric paper and to remain alkaline after separating from the ethereal fat solution. The corked tube is set aside, and in a few hours, at most, the greater part of the aqueous solution, now colored more or less yellow by the anatto, can be drawn from beneath the ether with a pipette, or by a stopcock below, in a sufficiently clear state to be evaporated to dryness and tested in the usual way with a drop of concentrated sulphuric acid.

Sometimes it is well to further purify the aqueous solution by shaking it with some fresh ether before evaporating it, and any fat globules that float on its surface during evaporation, should be removed by touching them with a slip of filter paper, but the solution should not be filtered because the filter paper may retain much of the coloring matter.

The dry, yellow, or slightly orange residue turns blue or violet-blue with sulphuric acid, then quickly green, and finally brownish, or somewhat violet, (this final change being variable according to the purity of the extract).

Saffron can be extracted in the same way ; it differs from anatto very decidedly, the most important difference being in the absence of the green coloration.

Genuine butter, free from foreign coloring matter, imparts at most a very pale yellow color to the alkaline solution, but it is important to note that a mere green coloration of the dry residue on addition of sulphuric acid is not a certain indication of anatto (as some books state), because the writer has thus obtained from genuine butter, free from foreign coloring matter, a dirty green coloration, but not preceded by any blue or violet-blue tint, * * * *

Turmeric is easily identified by the brownish to reddish stratum that forms between the ethereal fat solution and the

alkaline solution before they are intimately mixed. It may be even better recognized by carefully bringing a feebly alkaline solution of ammonia in alcohol beneath the ethereal fat solution with a pipette and gently agitating the two so as to mix them partially.

Estimation of Wood Pulp in Paper.—C. Wurster, Ber. d. deut. chem. Ges. 20, 808. Dimethyl-paraphenylene diamine has no action on cellulose, but colors finely divided woody fiber red. The amount of color given to a paper is proportioned to the amount of woody fiber it contains. By comparing the color obtained in this way from paper containing an unknown amount of woody fiber with other papers containing known amounts, quantitative results can be obtained.

Resorcinol as a Reagent for the Detection of Aldehydes.—Michael and Ryder, Amer. Chem. Jour. 9, 134.

“In testing for an aldehyde we recommend a solution of 1 part of resorcinol in 2 of absolute alcohol, then the addition of a small amount of the substance to be tested, and finally a few drops of strong hydrochloric acid. If no resin is formed, the solution, after standing several hours, is poured into water, when, if the substance contains any aldehyde, a resinous or crystalline precipitate should be formed. This test is of special interest, inasmuch as it distinguishes an aldehyde from a ketone, while such reagents as hydroxylamine and phenylhydrazine give tests for both these groups of substances. By combining the resorcinol test with one of the above, it may be ascertained whether the substance contains a ketone, as, if a substance gives the two last tests and not the first, it must evidently be due to the presence of a ketone.

Estimation of Starch.—A.V. Asbøth, Rep. anal Chem, 7, 299. 1 gm. of starch is weighed into a graduated flask holding 250 c. c., 150 c. c. water added and the flask heated for half an hour in boiling water, 50 c. c. baryta water is now added and the closed flask shaken for two minutes and the flask filled to the mark with 45 per cent. alcohol and allowed to cool. After cooling the volume is again made up to 250 c. c. by adding more alcohol. After the solution has cleared up 50

c. c. of the supernatant liquid is withdrawn with a pipette and the excess of baryta contained in it, over the amount needed to precipitate the starch is determined by means of deci-normal acid. The starch precipitate has the composition $C_{24}H_{40}O_{30}$, BaO. Care must be taken to protect the solution of baryta from contact with the air. The method gave results varying between 83.52 and 84.65 per cent. starch in wheat starch, 85.65 and 85.85 in maize starch, 79.87 and 80.43 in rye starch, and 77.27 and 78.65 in potato starch.

AGRICULTURAL ANALYSIS.

EDITED BY H. W. WILEY.

Comparative Estimation of Nitrogen in Milk by the Soda-Lime and Kjeldahl Methods.—Weiske (Versuchs-Stationen, 33, 310) shows that the Kjeldahl process with or without the use of permanganate of potassium gives better results for nitrogen in milk than one obtained by combustion with soda-lime.

Kreusler and Harnberger (Versuchs-Stationen, 31, 254) have shown that the soda-lime process gives constantly less nitrogen in milk than combustion by the method of Dumas. On the other hand the numbers obtained by the Kjeldahl moist combustion, agree so closely with those of the Dumas estimation as to leave nothing more in the way of accuracy to be desired.

Weiske obtained the following numbers by comparing the soda-lime with the Kjeldahl method:

<i>No. of Milk Sample.</i>	<i>By Will-Varrentrop, N. per 1000.</i>	<i>By Kjeldahl, N. per 1000.</i>
1	5.65	5.80
2	5.61	5.76
3	4.62	4.90
4	5.45	5.62
5	4.33	4.71
6	5.93	6.10

Estimation of Phosphoric Acid from the Ammonia Content of the Phospho-Molybdate Precipitate.—This proceed-

ing proposed by Jabert (*Chem. Zeit.* 2, p. 223) is designed to save time in phosphoric acid determinations and has been used especially in work with the Thomas Gilchrist slag. The molybdenum precipitate, after thorough washing with cold water, is brought into a flask with sodium hydrate and subjected to distillation. The distillate is collected in standardized sulphuric acid and the quantity of ammonia passing over determined by titration.

Natural and Artificial Digestion of the Nitrogenous Constituents of Fodder.—Pfeiffer, (*Zeit. f. Physiol. Chem.* 11, p. 1, et seq). The nitrogenous matter of the fodder and the nitrogenous matter, remaining in the feces of the sheep fed on fodder of known weight and composition was estimated as follows: The total dry substance was estimated in all cases at 105° in an atmosphere of dry hydrogen. The total nitrogen of the fodder and feces was determined by combustion with soda-lime. The artificial digestive experiments were carried on according to the two methods of Stutzer, first by treatment with pepsin solution and second by the successive use of pepsin solution and pancreas extract.

The pancreas extract is made as follows: 400 g. of the pancreas of a cow are ground in a mortar with sand, one litre of glycerine and the same volume of water are added, and the whole allowed to stand three days. To each litre of the resulting extract are added 5 c. c. chloroform and the vessel placed in a cool place where it will keep for several months. Of this artificial digestive liquid 100 c. c. are used for every 2 g. of the air dried fodder or feces. The necessary alkaline reaction is obtained by the addition of 100 c. c. of a 10 per cent. soda solution. After the digestion with the pepsin solution the material is not washed from the filter before treatment with the pancreas extract, but the filter paper is treated directly with the pancreas liquid. The amount of nitrogen in the filter paper should be determined by preliminary trial and then deducted from the total nitrogen obtained. The digestion with the alkaline pancreatic liquid is carried on in a water bath at a temperature of 38° to 40° and lasts from 8

to 10 hours. The residue is then filtered, well washed and the nitrogen in it estimated by the Kjeldahl method. The filtration takes place with great difficulty since the pores of the filter are easily stopped by the alkaline glycerine extract. Even when filtered under pressure much time is consumed, and all attempts to secure a substitute for the glycerine which would prove as effective and still be very easily filtered, have proved unavailing.

Chemico-Microscopic Estimation of Albuminoids in Plant Cells.—The method used by Krasser (Chem. Centralblatt, No. 12, March 26, 1887, p. 307) is as follows : The simple hydroxylated aromatic group is detected by Millon's reagent (acid mercuric nitrate.). Those atomic groups which by the decomposition of the albuminous bodies appear as asparagin or aspartic acid are detected by alloxan. Solid albuminoids are colored purple-red by alloxan. Tyrosin, asparagin and in general those organic bodies which contain the group CH_2 , CHNH , COOH give the same coloration. The test with alloxan must be made in the cold with a careful exclusion of ammonia. Free acids also hinder the alloxan reaction. The indifference of alloxan to coniferin and vanillin make the above described reaction more significant. Yet it must be confessed that no color reaction which is produced by albuminoids alone has yet been discovered. The action of the following additional reagents on albuminoids is also described.

Xanthoproteic acid ; Hydrochloric acid.

Raspail's reaction ; alkaline copper sulphate solution ; and sulphuric acid containing molybdic acid.

Alloxan is preferred to all the others for detecting albumen in hardened woody fibre.

Quantitative Estimation of Raffinose.—Raffinose occurs generally mixed with a large excess of sucrose as in the sugar beet. A method of estimating the amount of it present by double polarization has been proposed by Creydt (Zeit. d. Ver. f. Rúb. Z. Ind. 153, p. 80 ; Chem. Centralblatt, April 1887, p. 366).

Let the direct polarization of a mixture of sucrose and raffinose = A.

Let S = polarization due to sucrose and $1557 R$ = polarization due to raffinose.

(The specific rotary power of sucrose is $(\alpha)_d = 66.5$; of Raffinose $(\alpha)_d = 104.5$; ratio $1:1.57$.)

Let C = polarization after inversion. Then $C = 1.32 S + 1.57 R$. $O .493$. Here 1.32 indicates the difference in each degree of the original polarization and the polarization after inversion. Since sucrose polarizing 100° before inversion marks -32° , afterwards at $20^\circ C$. a difference of 132° ; and raffinose polarizing 100° before inversion makes $50^\circ .7$ afterwards at $20^\circ C$., a difference of $49^\circ .3$.

$$\text{Then } S = \frac{C - 0.493 A}{0.827} = \text{per cent. sucrose.}$$

NOTE.—This equation is obtained as follows: Multiply $A = S + 1.57 R$ by $.493$ which gives $.493 A = .493 S + 1.57 R .493$. Subtract from this $C = 1.32 S + 1.57 R .493$ and this leaves $.493 A - C = -.827 S$. whence

$$S = \frac{C - 0.493 A}{.827}$$

$$\text{And } R = \frac{A - S}{1.57} = \text{per cent. Raffinose.}$$

These two formulae give sufficiently exact results when no other optically active substances are present except sucrose and raffinose. If such other bodies are present the method is not applicable. In these cases the raffinose is estimated by first converting it into mucic acid by oxidation with nitric acid.

Within varying known quantities of raffinose, by conversion into mucic acid, a curve has been constructed, representing graphically the quantity of raffinose corresponding to a given point. When an unknown substance is examined the quantity of mucic acid is noted and the required amount of raffinose present determined by consulting the curve.

Fat in Milk.—Soxhlet (Milch Zeit. 16, p. 117), has described the use of a centrifugal machine, the principle of which is the same as I described in this Journal (Vol. 1, pp. 124 et seq). This method was first presented to the Chemical Society of

Washington, April, 1886, and described in full at the Buffalo meeting American Association for the Advancement of Science in August, 1886.

Estimation of Nitrogen in Manures Containing Nitrates.—Stutzer & Reitmaier, Rep. anal. Chem. 7, 4. A modification of the method of Iodlbaur. 1 gm. of the manure is treated in a flask with 25 c. c. water and evaporated to dryness in an air bath. This distributes the nitrates evenly throughout the mass. The drying is finished at 110°. After cooling 50 c. c. concentrated sulphuric acid, containing 20 gms. phenol per liter is added. This converts the nitrates into nitro phenol. After shaking for several minutes, 2 to 3 gms. zinc dust and 1 to 2 drops of metallic mercury are added and the mixture heated over the lamp for an hour and a half. This converts the nitro phenols into amido phenols, and then into ammonium sulphate. The operation is then completed in the usual way. See also Rep. anal. chem. 5, 232. H.

Estimation of the Specific Gravity of Butter and Other Fats.—J. Skalweit, Rep. anal. Chem. 7, 6. The author points out the value of a knowledge of the specific gravity of the same fat at different temperatures in determining its character. The determination is made by filling a piknometer with the melted and filtered fat and maintaining the temperature at 35 for 2–3 hours. The outside of the piknometer is cleaned by washing with light petroleum. The temperature is then raised to 50° and the piknometer cleaned and weighed as before. H.

Action of Phenyl-Hydrazin on Sugars.—(Emil Fischer, Berichte d. deut. chem. Gesell., 1887, p. 821.) Phenylhydrazin combines with the various sugars which reduce alkaline copper solutions to form compounds which are of analytical interest. The reaction is very delicate and the merest trace of sugar can be detected.

Mixed with dextrose in the cold phenylhydrazin forms dextrophenylhydrazin ($C_{12}H_{18}N_2O_6$). Crystallized from alcohol this substance forms colorless crystals which melt at 144° C., and are carbonized at a still higher temperature.

Phenylglucosazon forms the golden yellow crystals melting at 204° C. It is made by heating dextrose or laevulose with acetate of phenylhydrazin or a mixture of chloride of phenylhydrazin and sodium acetate. Its molecular formula is $C_{18}H_{22}N_4O_4$. Characteristic compounds are also formed with galactose, lactose, maltose, manitose, etc.

Sucrose is indifferent to its action. Fischer proposes to classify as sugars of the formula $C_6H_{12}O_6$ only those bodies which reduce Fehling's solution and form azones with phenylhydrazin.

The Lactocrite.—(Bul. No. 13, Chem. Div. U. S. Dept. of Agriculture, p. 101.) "The Lactocrite." This name is given to an instrument invented by De Laval designed to separate the fat in milk after appropriate chemical treatment.

"The test vessels used in this apparatus are cylindrical boxes made of silvered metal, with accurately ground hollow silvered stoppers. These stoppers are expanded at the bottom, and at the top are contracted, to end in a small hole. They are joined to a glass tube of small internal diameter. This tube is furnished with a jacket by which it can be screwed on the stopper, and this jacket carries two longitudinal slits, through which the divisions in the glass tube can be read. In the bottom of the jacket is a hole, so that the glass tube and metal stopper form a canal open at both ends.

"The centrifugal machine consists of a steel revolving disk. In the upper part of this there is a circular cavity, extending from which, like radii, are twelve holes to receive the test apparatus above described. These holes dip slightly downward. The disk is encased with a jacket having a removable cover which prevents a too rapid fall of temperature during the operation. By means of appropriate apparatus the disk can be driven at the rate of about 6,000 revolutions per minute.

"*Preparation of the milk.* In an ordinary test tube put equal portions of the milk to be tested and a mixture of twenty parts of concentrated acetic and one part of sulphuric acid. The test tube is closed with a cork in which is fixed a glass

tube, shaken, and heated for ten to fifteen minutes in a water bath with frequent shaking.

"The cylindrical box above described is now filled from the test tube, the metal cork forced in, whereby the apparatus is entirely filled, and the excess of milk forced out through the holes in the bottom of the jacket.

"The disk having been warmed to 50° to 60°C. by hot water, is now filled with these samples and revolved for three to five minutes at the velocity already noted. The temperature of the disk should not be allowed to fall below 50°C.

"At the end of this time the fat has completely separated and its volume can be read on the divisions of the glass tube. Each division is so arranged as to represent .1 per cent.

"Blyth has made a comparison of the results furnished by the lactocrite with those obtained by Adam's method. The results are given in the following table :

No.	Specific Gravity.	Total Solids. Per ct.	Ash. Per ct.	FAT.—Per Cent.		
				Lactocrite.	Adam's.	Difference
1.	1033.0	12.90	.80	3.40	3.44	— .04
2.	1031.0	14.12	.80	4.55	4.69	— .14
3.	1032.0	13.12	.77	3.60	3.57	.03
4.	1030.5	13.07	.74	3.90	3.99	— .09
5.	1032.0	12.98	.76	3.80	3.76	.04
6.	1031.5	14.27	.76	4.90	4.84	.06
7.	1032.5	13.84	.78	4.20	4.26	.06
8.	1030.5	13.00	.76	3.70	3.69	.01
9.	1031.0	13.51	.80	4.05	4.09	.04
10.	1034.0	11.76	.76	2.10	2.07	.03
11.	1035.0	9.99	.86	.45	.50	— .05

"The table shows the greatest differences between the two estimations to be .14 and the mean difference to be .05 per cent.

"It is estimated that with the lactocrite 48 determinations of fat in milk can be made in an hour."

New Methods for Estimating Fat in Milk.—Morse and Piggot (*Am. Chem. Jour.* 9, No. 2, pp. 108, et seq) describe a new method of drying milk preparatory to the extraction of the fat by benzine or ether.

About 20 g. dehydrated sulphate of copper are placed in a

porcelain mortar, and ten c. c. of milk are added, being careful to secure a complete absorption of the milk without allowing it to touch the mortar. The water of the milk is completely absorbed in a few minutes.

The mass is then rubbed up with some fine sand and transferred to an extraction tube. This tube which may be an ordinary chloride of calcium tube is stoppered with cotton wool and joined to a flask connected with a filter pump. The fat is now extracted by benzine, it being treated successively with twelve portions of benzine of 10–15 c. c. each. The flask containing the fat solution is then placed in a water bath and the volume reduced to 10 c. c. or less. Instead of weighing the fat it is saponified with an excess of semi-normal potash and the excess of alkali determined by standardized acid.

The quantity of potassium hydroxide estimated for one gram of butter is taken at 230 milligrams.

[NOTE.—The quantity of potash required for saponification depends largely on the percentage of volatile acids contained in the butter fat. Hence the assumption of a constant number to represent the quantity of potash required for one gramme of the butter fat likely to lead to an error. Thus normal butter has been found to contain as much as 6.5 per cent. volatile acids and to fall as low as 3.75 per cent, in these constituents. It appears to me that it would be better to determine the fats by weight in the above process. The use of dehydrated copper sulphate for drying the milk is certainly very ingenious.]

Another method of estimating the fat in milk has been suggested by Short (*Am. Chem. Jour.* 9, No. 2, pp. 100 et seq).

Two grams of milk are placed in a Hofmeister capsule (*schälchen*) filled partly with fine asbestos. The water is determined by drying for two hours in a chloride of calcium oven having a temperature of 110°C.

The capsule is then wrapped in extracted cloth, crushed and placed in an extraction tube. The moisture and fat in butter are determined in the same way.

NEW BOOKS.

“A NEW BASIS FOR CHEMISTRY,” by Thomas Sterry Hunt. S. E. Cassino, Boston, 1887.

In gaseous compounds the molecular weights are propor-

tional to the densities, but in the case of liquid and solid compounds the usually received molecular weights are those which they would have in the state of gas in the most simple condition, short of elementary dissociation. Vapor of sulphur at 1000° has a density corresponding to a molecule of S_2 , when cooled to 500° . The density is three times as great and corresponds to S_6 , when cooled still further, until condensation takes place we should expect still greater complexity in the molecule, whereas we are in the habit of regarding the sulphur molecule in all cases as S_2 . The many forms of sulphur with which we are acquainted, with specific gravities ranging from 1.926 to 2.05 show more or less condensation varying from about 1760 to 1874 S.

All bodies are referred to hydrogen as a standard of density. Thus one litre of water at 100° weighs nearly 14,622 times as much as an equal bulk of hydrogen at this temperature, so that if the molecule of $H=h_2$, that of water will be 1628 (H_2O) with an equivalent weight of 29,244. We may regard this as analogous to the olefine series of hydrocarbons in which the simplest members of the series are gases and the more complex liquids and solids. The different states of matter are thus regarded as different chemical compounds and the changes from one to the other as chemical changes. In the condensation of steam to form the water molecule we have great evolution of heat, and in the combination of the atoms of hydrogen and oxygen to form steam we have a similar action, differing only in degree and not in kind, save that in one case similar molecules and in the other dissimilar ones unite with each other. In tracing the change from ice up to the dissociated gases we find absorption of heat in melting, in vaporizing, and in dissociating, indicating in each case work of disintegration being performed. Mineral species, like calcite and aragonite, diamond and graphite, will have different molecules corresponding to different members of the solid olefines, thus for calcite the formulæ 775 to 805 $CaCO_3$, depending on the variety, and for aragonite the formulæ 860 $CaCO_3$, are given. J. B. M.

PAMPHLETS RECEIVED.—New Treatment of the Affections

of the Respiratory Organs and of Blood Poison by Rectal Injections of Gases. Published by James W. Queen & Co., Phila., 25 cents.

—New Apparatus for Treating Consumption by Gaseous Enemata, according to the method of Dr. L. Bergeon. James W. Queen & Co.

—Report on Experiments in the manufacture of Sugar at Magnolia Station, Lawrence, La. Third Report, by Guilford L. Spencer. Washington : Government Printing Office, 1887. From C. A. Crampton.

—The first number of a new weekly periodical called the "Chemical Trade Journal," edited by George E. Davis, published in Manchester, has made its appearance. Subscription price 10 shilling 6 pence. The new journal is very much like the Chemical News in size and general appearance. The editor, Mr. Davis, has had considerable experience as a manufacturing chemist, and is an energetic man. We wish the new venture success.

NOTES.

—According to Mactear (Jour. Soc. Chem. Ind. 6, 176) sodium can be produced by Castner's process for less than 25 cents per pound and potassium for very little more than this. If this proves correct it means cheap and pure alkaline salts for the analyst. These, especially the hydroxides, will be very welcome.

—Mr. J. S. C. Wells has examined "The Comparative Delicacy of some Qualitative Tests." He finds that mercury, lead, bismuth and copper can be detected with H_2S in solutions containing one part in a million of the metal. Silver in a dilution of one part in 800,000, and cadmium in a dilution of one in 200,000. The other tests commonly employed for these metals are generally much less delicate. (School of Mines Quarterly, July, 1887.)

—The Philadelphia bakers have been using chrome yellow

to replace yolk of eggs in cakes and buns, a number of deaths have resulted in consequence. One of the witnesses at the coroner's inquest stated that he thought probably 80 per cent. of the bakers there were in the habit of using chrome yellow.

—The State Agricultural and Mechanical College at Auburn, Ala., was burned on June 24. The fire broke out in the laboratory, and is supposed to have been caused by rats gnawing matches. Loss \$100,000, insurance \$30,000. The building will be replaced at once.

—E. Fischer and F. Penzoldt have examined the delicacy of the sense of smell, especially with reference to mercaptan and chlorphenol. They find that an ordinary nose can detect the presence of $\frac{1}{4,600,000}$ milligramme chlorphenol and $\frac{1}{460,000,000}$ milligramme mercaptan. They propose that mercaptan be employed in experiments on diffusion, the testing of ventilation, etc. Ann. d. Chem. **239**, 131.

—Mr. A. E. Outerbridge, Jr., finds that an accurate reproduction in cast iron of embroideries, lace, etc., may be obtained by placing the fabric against the face of the mould and casting directly upon it. The most curious feature of this discovery is that the carbonized lace remains flexible after this severe treatment and can be stripped off and used over again for the same purpose. (See Journal of the Franklin Institute, June, 1887.)

—Dr. Henry Leffman, editor of The Polyclinic (P. O. Box 791, Philadelphia), desires to obtain results of the new treatment of pulmonary consumption and phthisis by gaseous enemata, for publication in The Polyclinic.

—Prof. Wm. P. Mason has sent to the Chemical News, (55, 175) an account of an instance in which the drinking of diluted sewage from healthy persons caused sickness. He argues from this that " 'specific' germs are not essential to a sewage in order to make its presence in drinking water strongly objectionable." The analysis of the water gave 15000 parts free ammonia per million, 2800 albumenoid ammonia, 46000 chlorine and traces only of nitrates and nitrites.

—Artificial pepper, consisting of wheat flour and a little

Spanish pepper, *capsicum longum* has made its appearance in the German markets. See Chem. Zeit. 11, 507.

—F. Mylius finds that the blue “iodide of starch” consists of starch, iodine and hydriodic acid. Its composition is expressed by the formula: $(C_{24}H_{40}O_{20}I)_4HI$. (Ber. d. deut. Chem-Ges. 20, 688.)

—“It being desired to put sufficient ammonia into a solution to produce a reaction, the writer asked the instructor to smell it to see if there was sufficient. The instructor, who was a German, replied: ‘I say every time, yes; I have not yet sold my nose to the School of Mines.’ ”—(School of Mines Quarterly, July, 1887.)

—Mr. Chas. B. Green, lately assistant at the University of Illinois, has been appointed chemist of the Secaucus Iron Co., Secaucus, N. J. Mr. I. A. Bachman has been appointed chemist of a sulphuric acid works at Augusta, Ga.

—Mr. E. D. Campbell, chemist for the Ohio Iron Co., Zanesville, has been appointed chemist of the Sharon Iron Co., Sharon, Pa.

—NECROLOGY—Jean Baptiste Joseph Dieudonne Boussingault, the renowned chemist and agriculturalist, died in Paris on May. 12th, at the age of 85.

—In Munich, June 1, George Christian Wittstein. Wittstein prepared the index to Vols. 1–116 of Liebig’s Annalen, and wrote upon analytical chemistry, especially in its relation to pharmacy, botany and food supply.

=====THE=====

Journal of Analytical Chemistry.

QUALITATIVE ANALYSIS WITHOUT HYDROGEN SULPHIDE.*

BY I. A. PALMER.

CHEMISTS have long felt the need of some reagent which could be advantageously substituted for hydrogen sulphide in qualitative analysis. The inconveniences attending the preparation of hydrogen sulphide, its offensive odor, and the ease with which it decomposes when in water solution, render it one of the most troublesome and disagreeable reagents in the laboratory.

Several schemes of analysis have been proposed in which the use of hydrogen sulphide is dispensed with. Sodium hyposulphite has been suggested as a substitute, but the large separation of sulphur, the liberation of sulphurous acid and the tendency to oxidation, have prevented its successful use as a reagent.

About fifteen years ago Zettnow† published a scheme for qualitative analysis by which the metals were not converted into sulphide at all, but separated by other means, sulphuric acid being used as a group reagent for Ba, Sr, Ca, and Pb, and zinc to precipitate the heavy, easily reducible metals in the metallic state.

*Graduating Thesis 1887.

†Pog. Annal., 130, 324.

G. S. Eyster* has published a method of analysis which is, in part, a modification of Zettnow's scheme, but in which ammonium sulphide is used to precipitate the heavy metals. This scheme, although doing away with hydrogen sulphide, has not made the case much better. The use of ammonium sulphide presupposes the preparation of hydrogen sulphide. Besides, ammonium sulphide cannot be kept for any length of time without decomposing to such an extent as to be unfit for use in certain operations ; as in the precipitation of nickel.

The great trouble with both these schemes is that they are tedious and require very careful working in order to insure good results, facts which have prevented their general adoption in text books. It would seem, from our present knowledge, that the grouping as sulphides is the only method by which the metals can be separated with the speed and accuracy required in analytical processes. Hence, if we are to do away with hydrogen sulphide, we must use a reagent by which the metals can still be converted into sulphides.

Some time ago Th. Rosenbladt† published the results of some quantitative separations which he had made by using a solution of potassium thiocarbonate. This reagent he prepared by dissolving sulphur in carbon bisulphide and digesting the mixture for several days, with frequent shaking, with caustic potash solution. By this means he obtained an orange-red liquid, which precipitated some of the metals, apparently as sulphides, and retained others in solution, but which could be precipitated on continued boiling, or by the addition of acids. His experiments seem to have been conducted mainly for the purpose of finding a method for the separation of mercury from lead, bismuth, copper, silver and palladium, as he does not give any results obtained with the other metals, except that he states that the precipitates at first produced in nickel and cobalt solutions are soluble in an excess of the reagents.

Rosenbladt's paper suggested the thought that ammonia solution might be successfully used instead of caustic potash in the preparation of an alkaline thiocarbonate. Experiments made

*Amer. Chem. Jour., 7, 21.

†Zeit. anal. Chem., 26, 15.

with ammonia soon confirmed this idea, as, upon treating a mixture of carbon bisulphide and sulphur with ammonium hydroxide for several days with frequent shaking, a dark red liquid was obtained, which conducted itself in like manner as the reagent of Rosenblatt, with certain modifications that will be mentioned further on.

A few experiments performed with this solution made it seem probable that it could be advantageously used in qualitative analysis as a substitute for hydrogen sulphide. A more extended course of experiments was then performed with it, for the purpose of ascertaining its value as a reagent, and of devising, if possible, a scheme of analysis in which hydrogen sulphide could be entirely dispensed with.

Before beginning experiments with the different metals the reagent itself was examined. Prepared as stated above, it is a dark red liquid of a somewhat disagreeable odor, resembling that of ammonium sulphide. The color and smell, however, vary with the mode of preparation and the degree of concentration. The concentrated solution, in contact with an excess of carbon bisulphide, gradually deposits yellow crystals around the sides of the vessel, just at the point where the two liquids meet. These crystals look not unlike sulphur, but are insoluble in carbon bisulphide, and dissolve in water to a muddy, yellow fluid. Hydrochloric acid added to the water solution of the crystals produces a large separation of sulphur and a strong smell of sulphur dioxide, together with a small separation of carbon bisulphide. This indicates that the crystals contain thiosulphates in excess of the thiocarbonate present, as a smell of hydrogen sulphide would be noticed if the thiocarbonate predominated. This fact explains the formation of the crystals. The alkaline thiosulphates are almost insoluble in a strong solution of thiocarbonate. Hence, as the liquid grows more concentrated from the absorption of carbon bisulphide, the thiosulphates formed will gradually crystallize out at the junction of the two liquids, where, of course, the solution contains the most thiocarbonate. If the flask be shaken the crystals fall to the bottom and are protected by the carbon

bisulphide. As yet these crystals have not been thoroughly examined, but the above seems to be a rational explanation of their occurrence.

Regarding the reagent itself, it can be made in either of two ways. The first method is that given above. Made in this manner, and treated with hydrochloric acid, it gives a white precipitate of sulphur, carbon bisulphide separates out, and a smell of hydrogen sulphide is noticed. If any thiosulphates are present, the sulphur dioxide cannot be detected, as it is immediately decomposed by the hydrogen sulphide set free. This reaction seems to indicate that the solution contains an excess of ammonium thiocarbonate, together with some thiosulphates. The reagent can also be made by digesting carbon bisulphide with ammonium sulphide. If any of the latter reagent is at hand, this method is much shorter than the other, a few hours being sufficient to make a strong solution. This variety of the reagent naturally contains but little, if any, thiosulphate. The color is of a pinkish tinge, by which it can be easily distinguished from that prepared by the first method. Acidified with hydrochloric acid, but little separation of sulphur takes place, while large amounts of carbon bisulphide and hydrogen sulphide are liberated. The sulphur at first separated easily dissolves in the free carbon bisulphide formed, if the vessel be shaken for a short time.

This variety of the reagent does not seem to possess quite as great a solvent action for some of the sulphides as the former. It was found that a mixture of the two gave good results. There is danger of having too much sulphur in the reagent when it is prepared by the first method. If, however, the right proportions are taken, and the mixture allowed to stand some time in contact with an excess of carbon bisulphide, the thiosulphates will gradually separate out and the carbon bisulphide will be absorbed, producing a reagent which gives but a small separation of sulphur on treatment with acids.

The great advantage which this reagent possesses over hydrogen sulphide and ammonium sulphide lies in the fact that it lasts any length of time, and in fact improves with age, if kept in a stoppered bottle with carbon bisulphide.

Having obtained in this manner a large amount of the reagent, experiments were made with solutions of all the metals usually precipitated as sulphides in the course of qualitative analysis. The reagent was used in a rather concentrated form, as this facilitates the solution of some of the soluble sulphides. The tendency to oxidation is also lessened. In each case the metallic solution was made alkaline with ammonia, and ammonium chloride added previous to the addition of the thiocarbonate, as it was found that this is essential in order to obtain accurate separations in the case of mixtures of the different metals. The results of the experiments made with each metal separately are as follows :

Salts of gold give a yellowish-brown precipitate, difficultly soluble in excess of the reagent to a solution of a darker color than the thiocarbonate solution.

Platinum gives a brown precipitate, easily soluble in excess to a dark, yellowish-brown fluid.

Stannous salts give at first a brownish-yellow precipitate, easily soluble in excess to a solution of the same color as the reagent. With stannic salts the precipitate is yellow at first, also soluble in excess.

Antimony salts give an orange precipitate soluble in excess.

Arsenic gives a yellow precipitate, soluble in excess.

Copper gives a brownish-red precipitate, which dissolves completely in an excess of the reagent to a fluid of an intensely dark red color.

All of the above metals, in solution in an excess of the reagent, are reprecipitated on continued boiling, or by the addition of dilute acids.

Nickel gives a brownish precipitate, quickly soluble in excess to a very dark red solution, the color of which is visible even in cases of extreme dilution. When dilute hydrochloric acid is added to this solution, the nickel is at first precipitated, but completely dissolves in an excess of the acid, slowly in the cold, and quickly on warming.

Cobalt gives a black precipitate, soluble in excess to a solution of a darker color, even, than that produced by nickel.

The precipitate thrown down when dilute hydrochloric acid is added, dissolves but slightly in an excess of the acid, even on heating.

These two metals are probably converted into soluble thiocarbonates by the reagents. Continued boiling reprecipitates them as sulphides.

Mercury gives a black precipitate, insoluble in excess and in dilute acids. Rosenblatt says that potassium thiocarbonate retains the mercury in solution, from which it can be precipitated by means of a current of carbon dioxide passed through the solution. The precipitate produced by the ammonium reagent seems to be the sulphide.

Bismuth gives a blackish precipitate, insoluble in excess, but completely soluble in dilute hydrochloric acid, slowly in the cold, quickly, if the solution be warmed. If water be added to this solution a brown precipitate is thrown down, probably an oxysulphide.

Lead gives a black precipitate, insoluble in excess, but soluble in dilute acids under the same condition as those required for the bismuth precipitate.

Cadmium gives a yellow precipitate, insoluble in excess, but easily soluble in dilute acids, even in the cold. The precipitate is pulverulent and liable to go through the filter. If the liquid is heated to boiling and allowed to stand some time, however, the precipitate becomes more granular and easier to filter.

Zinc gives a finely pulverulent, light yellow precipitate, which tends to run through the filter, but which can be filtered all right, if treated as in the case of cadmium.

Manganese, in cold solution, dissolves in a large excess of the reagent to a dark red fluid, but is completely precipitated on boiling a short time as greenish-gray sulphide, sometimes brown.

Iron is not completely precipitated in the cold, but partly dissolves in excess to a dark, almost black solution. It is completely precipitated, on boiling a short time, as black sulphide.

Chromium is at first partly precipitated, but dissolves on heating to a dark fluid with a greenish tinge, from which it is reprecipitated on boiling as green hydroxide.

Aluminium is completely precipitated as hydroxide, insoluble in excess.

All of the above metals, except gold, platinum, tin, antimony, arsenic, mercury, aluminium, and possibly copper and chromium, are probably, either wholly, or partially, converted into thiocarbonates by the reagent. Most of these are decomposed on heating to boiling. The precipitates produced by bismuth, lead and cadmium do not seem to be decomposed so easily by heat, as they are soluble in dilute acids, even after boiling for some time. The easy solubility in dilute hydrochloric acid indicates that the precipitates are not sulphides.

It will be seen that the metals usually precipitated as sulphides can be divided into two groups, with respect to their deportment with the new reagent. In the first group, containing those metals which are precipitated by the thiocarbonate solution, are included mercury, bismuth, lead, cadmium, zinc, manganese, iron and aluminium. In the second group, the metals of which are soluble in an excess of the reagent, are included gold, platinum, tin, antimony, arsenic, copper, nickel, cobalt and chromium.

The precautions mentioned above, relative to heating and the addition of ammonium chloride, must be observed, however, in order to insure a good separation of the two groups.

The above experiments, together with others made with mixtures of the different metals, led to the following scheme for qualitative analysis. It is, no doubt, capable of improvement.

Gold and platinum, if present, are most conveniently removed from the solution by means of ferrous sulphate and ammonium chloride, before the addition of the thiocarbonate, and hence they are not included in the scheme :

I. Silver, lead and mercurous mercury are first removed and separated in the ordinary way. The acid filtrate is then neutralized with NH_4OH , NH_4Cl added, if but little HCl was present, and a large excess of the reagent added. The mixture

is then heated to boiling and kept in ebullition for a short time, more of the reagent being added, if necessary, to dissolve separated sulphur, and keep the Cu and Co in solution. The precipitate is allowed to settle, and the solution filtered hot. The precipitate is washed first with cold and then with hot water. Here will be found Hg, Pb, Bi, Cd, Zn, Mn, Fe and Al. Sometimes it is necessary to filter the solution twice in order to obtain all of the Zn and Cd on the filter.

In the filtrate will be found Sn, Sb, As, Cu, Ni, Co and Cr. This solution is now placed in the hood and boiled until all of the NH_3 is expelled. This will precipitate all of the metals, except possibly Cr, which may remain in solution, if the liquid is concentrated, and much ammonium salts are present.

II. While this solution is boiling, the precipitate containing the second group is examined. It is first treated with dilute HCl and warmed. The HCl dissolves all but the Hg. The residue is dissolved in aqua regia and tested for Hg with stannous chloride.

The acid filtrate containing the Pb, Bi, Cd, Zn, Mn, Fe, and Al is now boiled until most of the acid is expelled, and the Pb precipitated with dilute H_2SO_4 .

The filtrate from the $PbSO_4$ is boiled with a little HNO_3 , excess of NH_4OH added, and the solution again boiled. This precipitates the Bi, Fe and Al. The washed precipitate is dissolved in dilute HCl, the solution evaporated almost to dryness, and a large excess of water added. This will precipitate the Bi.

To the filtrate from the Bi OCl formed excess of NaOH is added, and the solution boiled. Fe will be precipitated as $Fe_2(OH)_6$, leaving Al in solution. The filtrate is boiled with excess of NH_4Cl , when a white precipitate will show the presence of Al.

The filtrate from the Bi, Fe and Al, containing the Cd, Zn and Mn is now boiled until all NH_3 is driven off and sufficient thiocarbonate solution added to precipitate the metals. The mixture is again boiled until all NH_3 is expelled, and then filtered, when the three metals will be found on the filter as sul-

phides. Acetic acid is then poured on the precipitate. This dissolves out the Mn, leaving the Zn and Cd on the filter. The acetic acid solution is tested for Mn with bromine water.

The zinc and cadmium sulphide are now dissolved in strong HCl ¹, and $NaOH$ solution added in excess. This precipitates the Cd, leaving the Zn in solution. The precipitate is tested on charcoal.

The filtrate is just neutralized with HCl , evaporated to small bulk, filtered, if necessary, from separated $NaCl$, made alkaline with NH_4OH , and excess of oxalic acid added. A white precipitate, slowly forming, shows the presence of Zn. Tested on charcoal.

III. The precipitate produced by boiling the original filtrate from the second group is next examined. It contains a large amount of separated sulphur, which can be removed by means of carbon bisulphide, after the filtering.

The precipitate is then digested with warm dilute HCl for some time. This dissolves the Ni and Cr, and some Co, leaving a residue containing the Sn, Sb, As, Cu and most of the Co.

The filtrate from the residue is made alkaline with $NaOH$ and boiled for some time. This precipitates the Ni, Cr and the small amount of Co as hydroxides. This precipitate is then fused with a mixture of Na_2CO_3 and KNO_3 , and the fused mass boiled with water. The Cr is thus extracted as alkaline chromate, which is tested with lead acetate.

The residue containing the Ni and Co is dissolved in dilute HCl and the solution neutralized with NH_4OH . It is then acidified with CH_3COOH and the Co precipitated with potassium nitrite.

The Ni is precipitated from the filtrate with $NaOH$, and tested with the borax bead.

The first residue containing the Sn, Sb, As, Cu and Co is now treated with concentrated nitric acid and the solution evaporated to dryness. The residue is boiled with water and a little HNO_3 . This extracts the As, Cu and Co, leaving the Sn and Sb as insoluble oxides.

The filtered solution is boiled with HCl, sufficient to decompose all the HNO_3 , and then placed in a Marsh apparatus with zinc and sulphuric acid. The As expelled is collected and tested in the usual way.

The zinc precipitates the Cu in the metallic state, and can be dissolved in HNO_3 and tested further if but a small amount is present.

The contents of the apparatus are filtered and the solution neutralized with NH_4OH , after which the Co is precipitated by the addition of acetic acid and potassium nitrite.

The insoluble residue containing the Sn and Sb is dissolved in strong HCl, and the two metals separated in the ordinary way by means of zinc and platinum.

IV, V. Ba, Sr, Ca, Mg, etc., will be found in the filtrate from the precipitate containing the third group. These metals are separated in the usual way, after the removal of any Cr, which may remain in solution, by means of NaOH.

The above scheme seems to be capable of rapid working, and can be operated with little inconvenience, the solutions being placed in the hood where the reagent is to be expelled by boiling, while the analyst, in the meantime, is occupied upon another part of the separation.

The author desires to express his thanks to Prof. Edward Hart for valuable suggestions in regard to the new reagent and its application to analysis.

Lafayette College, Chemical Laboratory, June, 1887.

VOLUMETRIC ESTIMATION OF PHOSPHORUS IN IRON AND STEEL.

BY EDWARD D. CAMPBELL.

THE method is based on the fact that stannous chloride reduces molybdic acid in a hydrochloric acid solution to molybdenum pentachloride which can be estimated volumetrically by means of potassium di-chromate, using ferrous chloride to

take up the excess of potassium dichromate and to act as an indicator. The standard solutions are made on the assumption that the phospho-molybdate precipitate has the composition $3(\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 22\text{MoO}_3 \cdot 12\text{H}_2\text{O}$ containing 1.685 per cent. phosphorus and 86.01 per cent. molybdic acid.

Method for Steel and Wrought Iron.—Take 1 gram, dissolve in 20-25 c. c. nitric acid 1.20 sp. gr. in a beaker about three inches high. Place on a wire gauze or hot plate and boil down rapidly about one-half; add 10 c. c. nitric acid, 1.42 sp. gr., continue the boiling and add about one-half gram of potassium chlorate gradually until manganese dioxide is precipitated. Remove the beaker and add a few drops of hydrochloric acid, 1.19 sp. gr. to destroy the excess of potassium chlorate and dissolve the manganese dioxide; add 5 c. c. nitric acid, 1.42 sp. gr. and boil down to 10-15 c. c. (A). Remove, add 10-15 c. c. of water and cool. Add ammonium hydrate .92 sp. gr. until the iron is precipitated, then redissolve in a slight excess of nitric acid, 1.42 sp. gr. The heat of formation of ferric and ammonium nitrates will raise the temperature of the solution to 60°-80°C. Now add 20 c. c. of molybdic acid solution previously filtered, shake well and allow to stand at 60°C. for ten minutes, when, if properly worked, the precipitate will be completely settled and the supernatant liquid clear. (If using non-Bessemer metal, more than 20 c. c. of molybdic acid solution will be needed, but not where the phosphorus does not exceed .150 per cent). When the phospho-molybdate precipitate has settled, filter with aid of a pump, wash with water containing 3 per cent. nitric acid, 1.20 sp. gr., then twice with water to remove the nitric acid. Transfer the funnel to another flask and dissolve the precipitate on the filter with dilute ammonium hydrate, washing the filter with water. Rinse the solution into a three-inch beaker and dilute to 70-80 c. c. Add 15 c. c. hydrochloric acid, 1.19 sp. gr., then 6-8 drops of stannous chloride solution; when the solution has passed from a very dark to a pale brown color, add another drop of stannous chloride solution, and if no increase of color occurs, enough has been added. Now add 10 c. c. of mercuric chloride, seven per cent. solution and stir well. Run in from a burette a mod-

erate excess of standard potassium dichromate, 1 c. c. = .0001 gm. phosphorus ; run in 12–15 c. c. when working on Bessemer metal. Add 10 c. c. of ammonium hydrate .92 sp. gr. to partly neutralize the large excess of hydrochloric acid and render the end reaction distinct. When this is done run in standard ferrous chloride, 1 c. c. = .0001 gm. phosphorus, 1 c. c. at a time, until a test is given for ferrous iron with potassium ferricyanide on a test plate. When a color is obtained titrate back the slight excess of ferrous chloride with standard potassium dichromate. The number of c. c.'s of potassium dichromate used less the number of c. c.'s of ferrous chloride gives the number used in oxydizing the molybdenum pentachloride to molybdic acid, and since 1 c. c. equals .0001 phosphorus if 1 gm. of metal was taken for analysis each c. c. of dichromate used equals .01 per cent. phosphorus.

Test Analysis.—Bessemer steel, phosphorus gravimetrically .089—.092 per cent. Volumetrically .092 per cent. Time, 35 minutes.

Method for Pig Iron.—Take 1 gram, dissolve in nitric acid, 1.20 sp. gr. in a three and one-half inch porcelain evaporating dish ; when the action has ceased add 5 c. c. hydrochloric acid, 1.19 sp. gr. and boil down rapidly nearly to dryness. When nearly dry lower the flame and continue to dryness, when the flame is increased again until all acid fumes have been given off. Remove, add 10 c. c. hydrochloric acid, 1.19 sp. gr., heat to solution, then add a little water and filter with aid of a pump ; wash. Rinse the solution into a three-inch beaker, boil, add 10 c. c. of nitric acid, 1.42 sp. gr., and boil down to 10–15 c. c. From this point continue as when working steel, beginning at the point marked (A).

Test Analysis.—Bessemer pig iron. Phosphorus gravimetrically .118 per cent. Volumetrically .121 per cent. Time 1 hour 35 minutes.

Test Solution of Molybdic Acid.—From the proportion $86.01 : 1.685 :: x : .1$ $x = 5.1044$ we get the amount of molybdic acid that must be used in 1000 c. c. in order that each c. c. shall equal .0001 gm. phosphorus. Hence, take 5.1044 grms. of molybdic acid, MoO_3 , dried at 120°C , dissolve in 200 c. c.

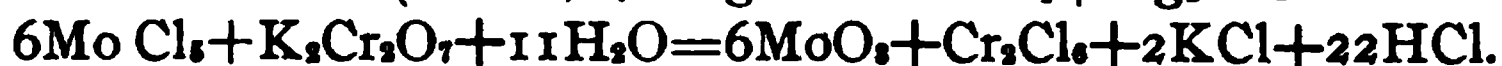
hydrochloric acid, 1.19 sp. gr., with heat. When dissolved, cool and dilute to 1000 c. c.

Potassium Dichromate Solution.— $\frac{n}{10}$ factor of molybdic acid, $\text{MoO}_3 = .01436$. $\frac{n}{10}$ factor of potassium dichromate = .004917. Hence, to make the potassium dichromate, $14.36:4.917::5.1044:x$. $x=1.7474$. 1.7474 grms. $\text{K}_2\text{Cr}_2\text{O}_7$ dissolved in 1000 c. c. water. 1 c. c. = .0001 gm. phosphorus.

Ferrous Chloride Solution.—Take 2 grms. of fine, pure iron wire, dissolve in dilute hydrochloric acid and standardize by potassium dichromate, 1 c. c. = .0001 gm. phosphorus.

Stannous Chloride Solution.—Stannous chloride, 20 grms. ; hydrochloric acid, 1.19 sp. gr., 35 c. c. ; water, 60 c. c. Place in a beaker and heat until the solution is perfectly clear.

REACTIONS.



NOTES ON BURETTES AND PIPETTES.

BY W. O. ATWATER AND C. D. WOODS.

IN connection with certain work in this laboratory some time since it seemed desirable to secure as accurate measurements of standard solutions as should be conveniently practicable. Results of a number of series of weighings of water delivered by pipettes and burettes of different forms, and with jets of different sizes led us to use very narrow burettes where accurate measurements are needed, a practice which several years' experience has appeared to us to justify. Some of the observations may be not unworthy of record.

The weighings were all made in glass-stoppered flasks of about 50 c. c. capacity. As a similar, empty, flask was at hand, it was used as a counterpoise though such refinement of precaution was really superfluous. Distilled water was employed for the measurements. The temperature of room

and water was practically constant during each series of determinations, though the temperatures of different series varied. As the determinations were intended simply to show the relative accuracy of delivery, it was not deemed necessary to reduce the results to uniform temperature.

Some difficulty was experienced in so cleaning the burettes and pipettes that they would drain without leaving drops on the walls. Of various reagents tried, a solution of strong caustic alkali was found most effective. The tube was filled with the alkali solution, allowed to stand a few minutes, emptied, washed with water, then with hydrochloric acid with alkali and with water, and the treatment repeated until after final rinsing with water, the acid or alkali solution could be drawn off in the usual way without adhering to the inside of the tube. Treating with potassium dichromate and sulphuric acid we also found effective. Since this work was done we have been favored by Messrs. Fauth & Co., philosophical instrument makers, of Washington, D. C., with the following statement of their method of cleaning tubes for spirit levels, which may be more efficacious than either of the above; we have not tested it.

"We clean the inside of our level tubes by first dipping them in nitric acid, then in distilled water, and finally in Squibb's sulphuric ether. Whether this process will answer your purpose we are not prepared to say. It serves ours perfectly."

We have noted that when a burette has been rinsed with acid, large drops of water have adhered to the sides, but when it was rinsed with alkali the quantity of liquid that adhered to the side was hardly enough to be visible. Whether this is to be explained by assuming that the material which held the water to the glass was fat we cannot say. Sometimes when the burettes have been treated with strong alkali and then with acid without rinsing the alkali out with water, the water has seemed to adhere more than before. Perhaps this may have been due to the saponification of fats by the alkali and precipitation of the fatty acids upon the glass when the stronger acid was added. But whatever the explanation may be we have found that to insure accurate delivery of solutions

from our burettes it is necessary to keep them clean inside and that for this, keeping them covered does not suffice.

Experiments with Pipettes.—Presuming that a given quantity of liquid might be most accurately and conveniently measured off by use of an overflow pipette, such as are employed in measuring standard solutions for silver assays, the following tests were made with pipettes of different forms. The pipette was in each case fastened in a perpendicular position. The water was introduced at the bottom, that which flowed over the top being caught by a small sponge. When the pipette was full, the top was closed by the finger, care being taken not to touch the sides, the drops adhering to the outside at the bottom were wiped off and the water then allowed to flow into the weighing flask. Pipettes of six different forms and designated as A, B, C, D, E, and F, were tried as follows:

Pipette A was of straight glass tubing, about 10 mm. internal diameter and 125 mm. in length. It was drawn out at both ends, the lower end making a jet rather wider than we have ordinarily seen used for burettes though not as wide as is often found in pipettes.

Pipette B was of the same tubing as A, but only 75 mm. long and had a finer jet so that the contents flowed out more slowly. The jet was as fine or finer than we have commonly seen used for burettes.

Pipette C was a duplicate of A, except that the jet was finer even than that of B.

Pipette D had a large spherical bulb, the lower end being a tube about 20 mm. long. The jet was of ordinary size. The water adhered to the inside of the tube, and as appeared to the eye, in varying amounts.

Pipette E was like D except that the tubular prolongations of the spherical bulb above and below were as short as practicable.

Pipette F was made from an ordinary 25 cc. pipette consisting of a tube with a cylindrical bulb. The lower tube was cut off near the bulb and drawn out to a very fine jet.

The weights of water delivered are stated in Table I, herewith :

TABLE I.
WATER DELIVERED BY PIPETTES OF DIFFERENT FORMS.

<i>Designations of Pipettes</i>	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
<i>Forms of Pipettes.</i>	<i>Tube, straight sides. Coarse jet.</i>	<i>Tube, straight sides. Finer jet.</i>	<i>Tube, straight sides. Very fine jet.</i>	<i>Spherical bulb, short delivery tube. Ordinary jet.</i>	<i>Spherical bulb, short delivery tube. Ordinary jet.</i>	<i>Cylindrical bulb, short delivery tube. Fine jet.</i>
<i>Observed Weights of Water Delivered.</i>	<i>Grams.</i> 20.066 20.071 20.078 20.085 20.095 20.085 20.088 20.087	<i>Grams.</i> 12.052 12.076 12.065 12.049	<i>Grams.</i> 20.153 20.157 20.155 20.148 20.148 20.150	<i>Grams.</i> 27.623 27.557 27.607	<i>Grams.</i> 27.539 27.550 27.563	<i>Grams.</i> 20.994 20.997 20.994 20.992 20.996
<i>Extreme variation in Observations</i>	0.029	0.027	0.009	0.066	0.024	0.005
<i>Maximum Probable Error.</i>						
<i>For Total Water Deliv'd</i>	0.015	0.014	0.005	0.033	0.012	0.003
<i>For 10 c. c. " "</i>	0.007	0.011	0.002	0.012	0.004	0.001

The pipettes with the finest jets, i. e., those delivering most slowly, gave the most uniform, and, it is to be presumed, the most accurate results. The two forms, C a straight cylindrical tube, and F the ordinary bulb pipette with the delivery tube cut off, both with fine jets, were as accurate as could be desired for ordinary use.

Experiments with Burettes.—For the trials recorded below, three burettes were used, one, A, of ordinary width, about 12 mm. internal diameter, and two, B and C, very narrow, about 5 mm. diameter. The jet of A was rather fine, and those of

B and C very fine, the latter delivered only about 3 to 5 c. c. per minute. With larger jets and more rapid flow water was sometimes left in small drops on the sides of the tube and even when no drops were visible some adhered to the sides and gradually ran down after the out-flow had ceased so that the surface of the water within rose on standing. As would be expected, the amount of this after-flow was greater, the greater the length of the emptied column, the more rapidly the water was drawn off, and the longer the time, up to a certain point, that elapsed between the stopping of the out-flow and the reading. The cleanness of the tube was also an important factor of the amount of after-flow. But with the very narrow tubes and fine jets, especially when the tubes were clean, this after-flow was extremely small. With rapid delivery the sides did not seem to drain evenly, even when the tubes were most carefully cleaned and considerable time was allowed for the after-flow. The weighings under these conditions showed wide variations. Despite all precautions to keep the inner surface free from dust and dirt, occasional cleaning was found essential to the greatest accuracy.

With the 50 c. c. burette of ordinary width, three series of trials were made. The results are given under A₁, A₂, A₃, in Table 2. In the series A₁ the burette was supported over the working table and the readings were taken from the bottom of the meniscus without any aid to reading or means to make certain that the eye was on the level of the meniscus. In A₂, the burette was securely fixed in front of a window and the eye brought to the proper level by sighting at marks on a building opposite. The outline of the meniscus was made sharper by an ordinary reflector of black and white paper. In A₃ the readings were made with an Erdmann's float. The narrow burettes B and C, were fixed perpendicularly in the window in like manner and the readings taken from the bottom of the meniscus without any aid except the marks on the opposite building or strips of paper pasted on the window glass 30 cm. from the burettes. Table 2 gives results of observations.

TABLE II.

WATER DELIVERED BY BURETTES OF DIFFERENT WIDTHS.

<i>Internal Diameter of Burettes.</i>	<i>Ordinary Width. About 12 mm.</i>			<i>Very Narrow. About 5 mm.</i>	
<i>Designation of Burettes.</i>	<i>A</i>			<i>B</i>	<i>C</i>
<i>Readings made by</i>	1	2	3	<i>Meniscus, with sights for leveling. Very fine jet.</i>	
	<i>Meniscus, without sights, for leveling.</i>	<i>Meniscus, with sights, for leveling.*</i>	<i>Float.</i>		
<i>Observed Weights of Water Delivered.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
	9.9745	9.9680	9.9000	5.0195	5.0160
	9.9535	9.9620	9.8950	5.0200	5.0160
	9.9650	9.9655	9.8950	5.0195	5.0155
	9.9700	9.9590	9.8970	5.0195	5.0150
		9.9585	9.8940	5.0190	5.0160
		9.9635	9.8980	10.0380	10.0300
		9.9610	9.8985	10.0375	10.0290
		9.9585	9.8995	10.0390	10.0315
		9.9565	9.8935	10.0375	10.0300
		9.9540	9.8980	10.0380	10.0290
<i>Extreme variation in ob- servations</i>	0.0210	0.0140	0.0065	0.0015	0.0025
<i>Maximum probable error for 10 cc.</i>	0.0105	0.0070	0.0033	0.0008	0.0013

Fresenius states that when pipettes are held in the hand and filled and emptied with the greatest care, the same 10 c. c. pipette will show differences of 10 mgm. and one of 50 c. c. differences of 40 mgm. in the weights of water delivered, but that if the pipette is fastened and the out-flow regulated by a pinchcock and jet, (thus making it equivalent to a very narrow burette) the differences with a 50 c. c. pipette may be reduced to 5 mgm.¹ This accords with the figures of Tables 1 and 2.

*Under surface of meniscus rendered more distinct by "reflector" of black paper on white background held behind burette.

1. Quant. Anal., 1875, p. 38.

Viewed with reference to the two most important factors of accurate measurement with burettes and pipettes, accurate delivery and correct reading, the above and other observations have led us to the following very simple, and doubtless in no way new, conclusions.

1. Leaving temperature out of account, uniformity and accuracy of delivery depend upon the completeness with which the liquid is removed from the inner walls of the tube. The amount of adhering liquid is greater, the greater the interior surface to be drained, the greater the amount of dirt, grease, etc., on this surface, the more rapid the out-flow, and the shorter the time allowed for the after-flow, i. e., for the adhering liquid to drain down. When the tubes are not clean and the delivery is rapid the amount of adhering liquid may be so large and so variable as to materially affect the measurements. But with clean tubes and narrow jets the uniformity and hence the accuracy are all that could be desired.

2. With a float, or, as is more convenient, a simple device such as a black and white reflecting surface of paper held behind the burette and sights to insure that the level of the eye shall be the same as that of the meniscus, or, indeed by using proper care without float or other help reasonably accurate reading is easy even with burettes of ordinary width.

3. With very narrow burettes, well cleaned and provided with fine jets, it is easy without float, reflector, sights, or other helps for reading, to make measurements with a probable maximum error of .001 to .002 c. c. in 10 c. c. For accurate measuring of small quantities of solutions therefore, the narrow burette is decidedly advantageous.

In the determinations of nitrogen by the soda-lime method we have found it convenient to employ very concentrated solutions of standard acid. For this we have, after some years experience settled upon a 10 c. c. burette of about 5 mm. internal diameter graduated to .05 c. c. For standard alkali which we make more dilute we employ a somewhat wider burette. Since the narrow burettes of ordinary thickness are apt to get broken, we find it advisable to have them made of very

thick glass. Burettes and pipettes made by H. Geissler's Nachfolger, Bonn, and by Emil Greiner of 79 Nassau St., N. Y., have proven very satisfactory.

For the ordinary work of analysis, burettes of the usual width, when they are kept clean and when the measurements by which they are calibrated and those in the ordinary routine of analysis are made in the same way, give tolerably good results, it is only when especial accuracy is desired that the narrow burettes and the precautions above suggested, (regarding cleanness of the burettes and either slow drawing off of the solution through narrow jets or other means to avoid error from the after-flow) are needed. Of course, the greater dilution of solution which may be used in the wider burettes compensates more or less completely for the larger error involved in their use. But where, for the sake of sharpness of the color reaction or for other reasons, as for instance, to avoid pressure on the combustion tubes, it is desirable to use very small quantities of concentrated solutions, the narrow burettes offer decided advantages.

Chemical Laboratory Wesleyan University.

VINEGAR ANALYSIS.

BY DR. BENNETT F. DAVENPORT, LATE VINEGAR AND MILK INSPECTOR FOR
THE CITY OF BOSTON.

SINCE several of the States have passed statutes requiring that vinegar, to be sold as cider vinegar, shall be the legitimate and exclusive product of pure apple juice; and should have attained to at least an acidity equivalent to a certain percentage of acetic acid, and contain not less than a given amount of cider vinegar solids, easy practical methods for determining these requirements have become of special interest. In the laboratory of the expert the percentage of acidity is best determined by the titration of 6 gms. of the vinegar with a normal solution of caustic alkali, using phen-

olphthalein as the indicator. The number of c. c. of the solution used being the desired percentage. The residue is best made by the evaporation of 10 gms. of the vinegar in a flat bottom platinum capsule upon a water bath.

But for commercial purposes simpler means are applicable which are but little less exact. As the limits set by the statute are in per cents by weight, the portion of vinegar taken for the tests should, for perfect accuracy, be also taken by weight; that is the quantities of 6 and of 10 grammes are to be taken for the tests of strength and of residue; but as taking it by measure, if of about the ordinary atmospheric temperature of 60 to 70 degrees F. will make the apparent percentage at most only 1 to 2 per cent. of itself greater than the true, that is will make a true 5 per cent. vinegar appear to be, say from 5.05 to 5.10 per cent., measuring proves in practice to be accurate enough for all common commercial purposes, and therefore the quantities of 6 and of 10 cubic centimeters by measure may be taken in place of as many grammes. For the acidity determination, therefore, dealers can well use an improved form of Acetometer made as follows: A glass tube with a bore of about the size of the tip of the little finger is closed at one end. At the height of 6 c. c. above the closed end the mark of 0 per cent. is placed, and above it each c. c. and subdivision of tenths are marked up to 10 c. c. but with the sign of per cent. in place of c. c. For use the tube is filled with the vinegar to be tested up to the 0 per cent. mark. After a drop of the tincture of phenolphthalein has been added the normal solution of caustic alkali is cautiously added, with repeated admixture of the contents of the closed and inverted tube, until at last a single drop causes a permanent pink color in the mixture. The height of the fluid within the tube upon its graduation gives then the percentage of acidity.

There are certain characteristics peculiar to the residue of a pure cider vinegar, the principal of which are the following: It will be about three per cent. in weight, and never less than two per cent. It is always soft, viscid, of apple flavor, somewhat acid and astringent in taste. Taken up in a clean loop

of platinum or of iron wire and ignited in a colorless Bunsen gas lamp flame it imparts to it the pale lilac color of a pure potash salt, without any yellow due to sodium being visible ; and the ignited residue left in the loop of wire will be a fusible bead of quite a good size, and will have a strong alkaline reaction upon moistened test paper, effervescing briskly when immersed in an acid. The presence in a vinegar of the *slightest* trace of any free mineral acid will prevent the ignited residue having any alkaline reaction, or effervescing with acids. The presence of any practical amount of commercial acetic acid added to "tone up" the strength of the vinegar, will cause the igniting residue to impart another color to the Bunsen flame, and the residue itself will have a smoky, pyroligneous taste or odor. Any corn glucose used in the vinegar will cause its residue when ignited to emit the characteristic odor of burning corn ; and as the last spark glows through the carbonized mass, to usually emit the familiar garlic odor of arsenic. For the common oil of vitriol usually used in the production of glucose is now mostly derived from pyrites, which almost always contain arsenic. A glucose vinegar which has been made without vaporizing the alcohol after the fermentation of the glucose will also have a strong reducing action upon a copper salt in an alkaline solution, and also will give a heavy precipitation of lime with ammonium oxalate. A true malt vinegar always contains phosphates, and a wine vinegar cream of tartar. The presence of any acrid vegetable substance in a vinegar is known by the residue having a pungent taste, especially if before the evaporation the vinegar has been exactly neutralized with soda.

In a pure apple cider vinegar hydrogen sulphide gas will not cause any discoloration, nor will the addition of a solution of either barium nitrate, silver nitrate, or ammonium oxalate cause anything more than the *very slightest* perceptible turbidity. But the addition of some solution of lead acetate will cause an immediate voluminous and flocculent precipitation, which will all settle out in about ten minutes,

leaving a clear fluid above. In most of the so-called "apple vinegars" brought into this market from other States, made largely from the repressings of fermented pumace, the addition of some of this lead solution will cause but a slight turbidity, without any precipitate settling out for several hours, and even then the precipitate will not be of the same appearance as in apple cider vinegar.

Sophistications of cider vinegar that will not be detected by some one or more of the above given tests are not likely to be met with, for the simple reason that they are not profitable. To translate percentages of acid strength into the old commercial terms of grains of soda bicarbonate per troy ounce, the per cent. may be multiplied by 6.72; or, vice versa, divide the grains by the same factor. To reduce it into grains of potash bicarbonate, 8 would be the factor to be used in like manner.

RAPID FILTERING APPARATUS.

BY CLEMENS JONES, B. S.

THERE are comparatively few technical laboratories equipped with rapid filtering apparatus. In the course of mere routine analysis, and in general, time is a valuable factor, and the rapidity with which filtration can be done not only increases what might be called laboratory capacity, but in avoiding the ordinary tedious manipulations saves patience, and in many cases secures better results. Probably some time honored prejudices have unconsciously exerted against their introduction, but for nearly every ordinary purpose the filter pump and convenient apparatus will adequately fill every requirement. In the use of the apparatus here to be described unsuccessful filtration is of the rarest experience. Where strong suction is employed—as that obtained from a Richard's vacuum pump—a receiver supplied with suitable valves; a vacuum gauge and the selection of proper filter paper will obviate all difficulty.

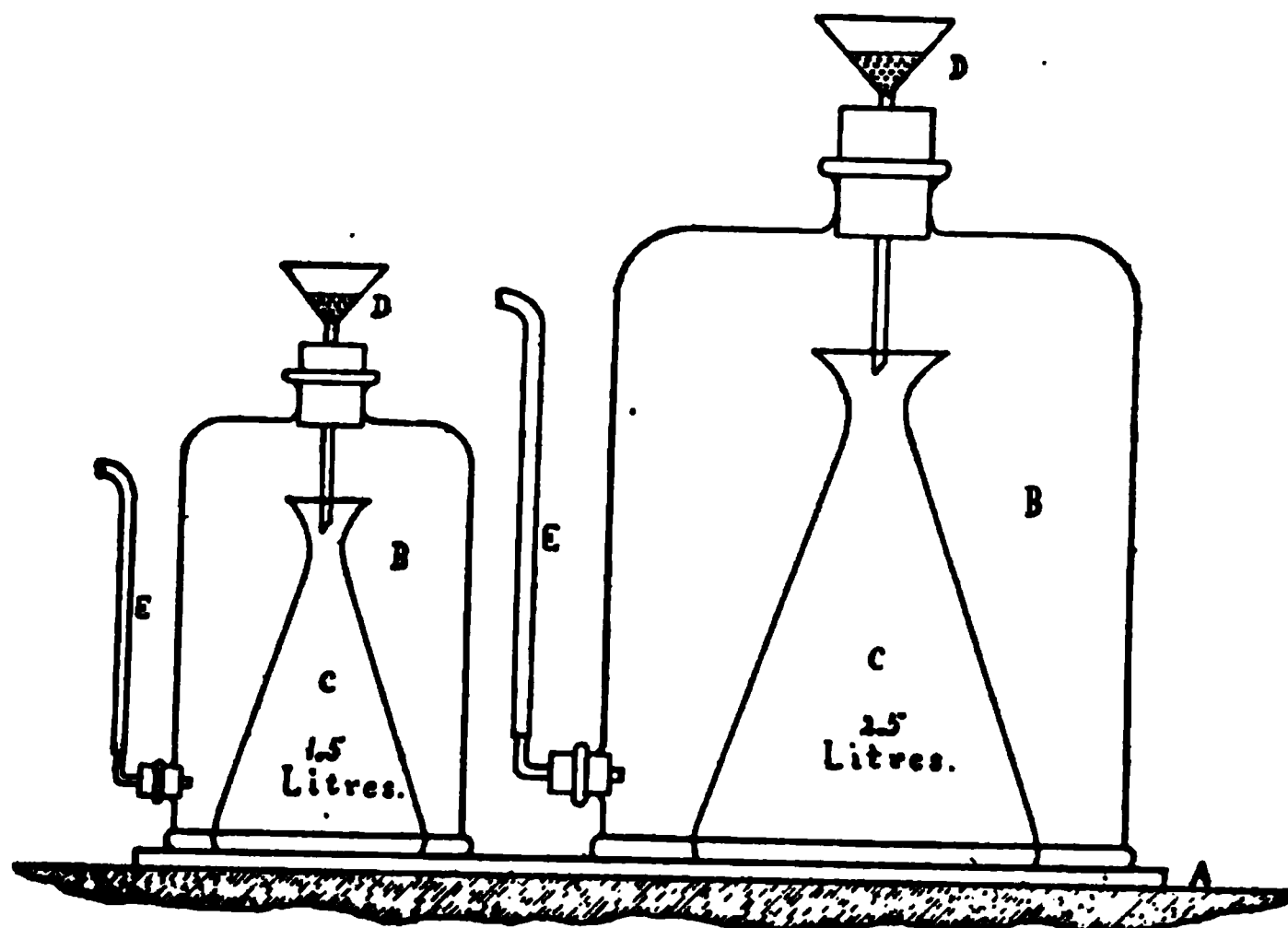


Figure 1.

Figure 1 shows an arrangement of a heavy glass plate, A ground to fit the bell jars B of two or more sizes. The funnels D have accurately fitted platinum cones with small perforations. C are Erlenmeyer flasks and E connections with the system of vacuum pipes, which are controlled by independent valves conveniently placed.

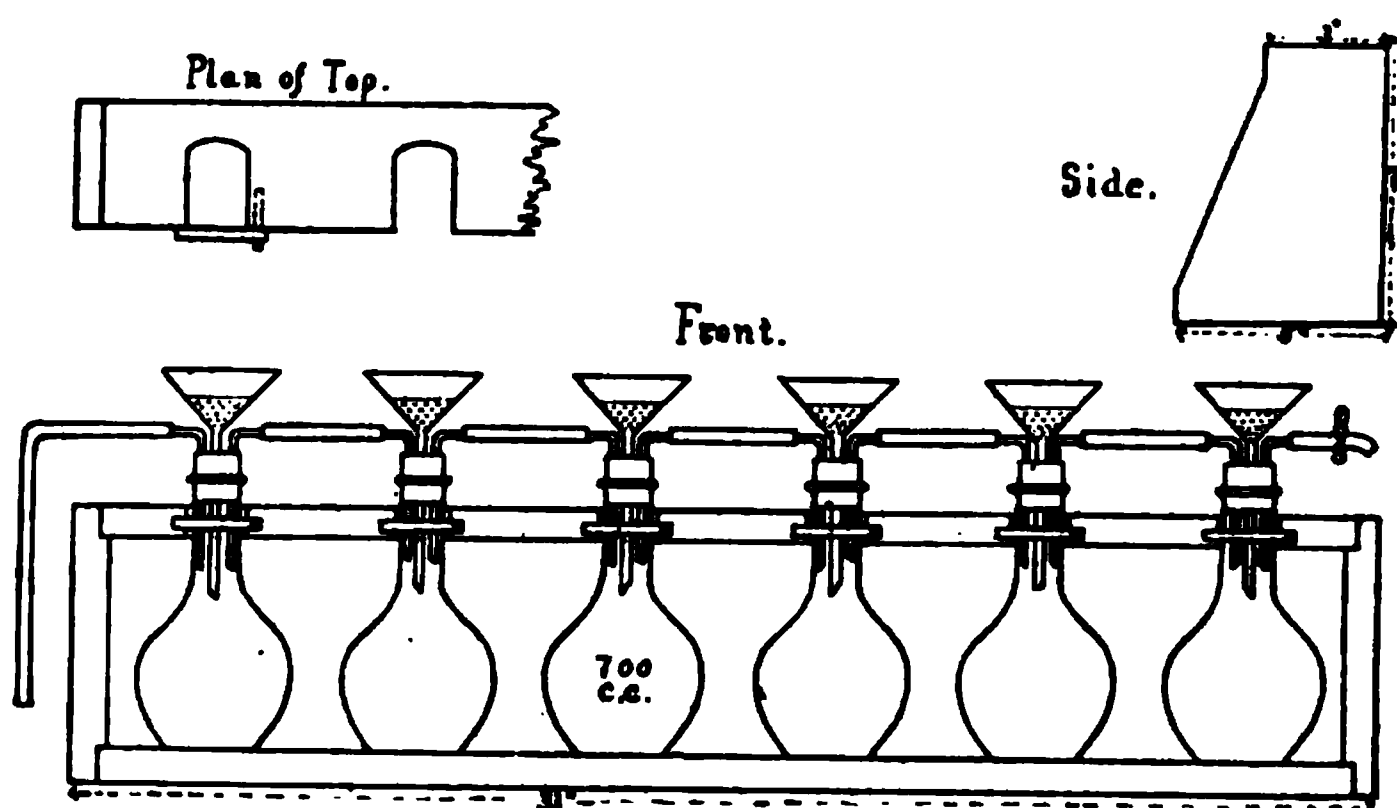


Figure 2.

Figure 2 shows an arrangement of heavy Bunsen filtering flasks formed into a battery by a light strong frame of wood, of which the details are represented. Each flask is provided with a perforated platinum cone. The rubber corks have three holes. Pieces of rubber tubing connect the elements of this very useful battery, which permits any one flask to be thrown out of circuit, leaving intact the rest of the series.

The cuts are explanatory of the rest of the contrivance.

NOTE BY THE EDITOR.—The arrangement shown in Figure 1 has been in use in the laboratory of Lafayette College since 1874 and was introduced by Dr. Charles McIntire, then Adjunct Professor of Analytical Chemistry. So far as I am aware, however, the apparatus has never been described in the journals.

ANALYSIS OF TWO MANGANESE MINERAL WATERS.*

By F. G. Novy.

As the title indicates these waters contain notable quantities of manganese and on that account it is desirable to place their analyses on record. The waters come from Kennedale, Texas, a small village a few miles from Fort Worth. At this place there are three wells within a short distance of each other; one of which (No. 1) has quite a local reputation as a cathartic. Water from this well has been on sale at Fort Worth for the past year or two, and is also being shipped to neighboring localities. The wells are rather shallow, perhaps not more than thirty feet in depth. The waters are clear, possess a strong saline taste and are acid in reaction. The water of only two of these wells was analyzed and the results obtained are here given.

The manganese was separated from the iron and aluminum by the basic acetate process and precipitated by bromine. The precipitate of peroxide was redissolved and reprecipitated to insure separation from any calcium that may have come down with the first precipitate.

The other constituents were determined in the usual manner.

* Read at the New York Meeting of the American Association for the Advancement of Science.

	<i>Water No. 1.</i>		<i>Water No. 2.</i>	
	<i>Grains per U. S. Gallon.</i>	<i>Grams per liter.</i>	<i>Grains per U. S. Gallon.</i>	<i>Grams per liter.</i>
Iron (Fe)	.245	.0042	3.266	.056
Aluminium (Al)	.268	.0046	7.045	.1208
Manganese (Mn)	1.438	.0247	5.511	.0945
Calcium (Ca)	38.104	.6534	42.193	.7235
Magnesium (Mg)	40.648	.697	20.382	.3495
Sodium (Na)	201.920	3.4624	47.191	.8092
Potassium (K)	traces		traces	
Strontium (Sr)	slight tr.		good tr.	
Ammonium (NH ₄)	traces		traces	
Chlorine (Cl)	250.18	4.290	89.52	1.535
Phosphates (PO ₄)			good tr.	good tr.
Sulphuric acid (SO ₄)	339.498	5.8215	186.724	3.202
Silica (SiO ₂)	4.32	.0740	6.13	.1051
Total	876.621	15.0278	407.962	6.9956

Nitrites and nitrates were absent. No. 1 possessed a hardness of 23° Clark's scale, whilst No. 2 had a hardness of 75°.

The following table represents the probable combinations of the elements determined above. The total is a trifle higher than the above and that is due to the iron and alumina being combined with sulphuric acid, although the amount of the latter as determined was insufficient for this purpose.

	<i>Water No. 1.</i>		<i>Water No. 2.</i>	
	<i>Grains per U. S. Gallon.</i>	<i>Grams per liter.</i>	<i>Grains per U. S. Gallon.</i>	<i>Grams per liter.</i>
Sodium chloride.	412.87	7.0797	119.76	2.0536
Calcium "			26.53	.4549
Sodium sulphate.	123.15	2.1117		
Calcium "	129.55	2.2215	110.87	1.9012
Magnesium "	203.24	3.485	101.91	1.7475
Manganese "	4.00	.0685	15.31	.2625
Aluminium "	1.70	.0291	44.62	.7651
Ferric "	.875	.015	11.66	.200
Silica.	4.32	.074	6.13	.1051
Total	879.705	15.0845	436.79	7.4899

Of the 187 analyses of mineral springs as reported in Dr. A. C. Peale's "Lists and Analyses of Mineral Springs of the United States," 1886, about one hundred are recorded as containing traces of manganese. Sixteen analyses record the presence of quantities of manganese salts ranging from 0.44 to 2.83 grains per gallon. Beyond this limit, only one spring, the Middletown Spring of Vermont, is reported to contain 9.41 grains of the carbonate.

The water of well No. 2 is therefore interesting, as containing the *largest quantity of manganese* yet reported upon, viz.: 15.31 grains.

UNIVERSITY OF MICHIGAN, AUGUST, 1887.

REPORT ON METHODS OF STATING THE RESULTS OF WATER ANALYSES.

At the Buffalo meeting of the American Association for the Advancement of Science a paper on this subject was read before the Chemical Section by Prof. W. H. Seaman, embodying the report presented to the Washington Chemical Society by a committee of that society. Some of the results arrived at by that committee, and their recommendations, are given in the following extracts from that report.

After giving a "list of forty-two methods of statement or expression, based on an inspection of about a thousand analyses," and noting that "in some places three scales were found in the same table, a part expressed as grains per gallon, another part as milligrams per litre, and the hardness in Clark's degrees," the report goes on to say:

"These can nearly all be reduced to one or another of four common methods of expression as detailed by Nichols, viz:

1st. Grains per English or imperial gallon (277 cubic inches or 10 lbs. = 70000 grains of pure water.)

2d. In grains to the U. S. or wine gallon (231 cubic inches = 58372 grains of pure water.)

3d. On a decimal basis, as parts per 100, 1,000, 1,000,000.

This is generally used in France and Germany, also in the Reports of the Rivers Pollution Committee of Great Britain, and in this country in reports of the National Board of Health and of many State Boards of Health.

4th. As so many milligrammes to the litre. (This would be the same as parts in 1,000,000 if the water had the same density as pure water.)

“After careful consideration the committee would recommend the following conclusions, viz :

1st. That water analyses be uniformly reported in parts per million or milligrammes per kilogramme, with the temperature stated, and that Clark's and all other systems be abandoned.

2d. That all analyses should be stated in terms of the radicals found, whether elementary or compound.

3d. The constituent radicals should be arranged in electrochemical series, the positive radicals first.

4th. The combinations deemed most probable by the chemist making the analysis should be stated both by symbols and by name.”

After some discussion of the matter the following committee of the Chemical Section was appointed to report for the consideration of the section at its meeting in 1887 a scheme for a uniform method of stating the results of analyses of both mineral and potable waters: Professors G. C. Caldwell, J. W. Langley, W. P. Mason, J. R. Myers and R. B. Warder.

This committee, concluding that the scale which would be convenient and suitable for a mineral water would if applied to a potable water involve the use of inconveniently small decimals, recommended the adoption of two scales, and, furthermore, as will be seen on comparison of their recommendations with those of the committee of the Washington Chemical Society of many of the features of that report.

I. Scheme for a mineral water.

The composition shall be expressed in parts per thousand.

The number of parts per thousand shall be given of each electropositive or basic element, K, Na, Li, Ca, Mg, Fe”

(Fe,)'' etc., and of each electronegative or acidic element, Cl, Br, I, S, etc., that may reasonably be supposed to be combined directly with an electropositive element, all these elements being arranged in the order of their electro-chemical character, the electropositive first. The remaining portions of the electronegative elements shall be given together with all the oxygen of their salts, as in the present generally accepted empirical formulas of those salts, such as SO_4 , PO_4 , CO_3 , etc.

The number of cubic centimetres per litre shall be given of CO_2 , H_2S , etc., expelled on boiling.

The combinations deemed most appropriate by the chemist making the analysis shall be stated both by symbols and by name.

II. Scheme for a potable water.

The composition of the water shall be expressed in parts per million (milligrammes per litre) as follows :

Total solids	
Chlorine	
Nitrogen expelled on boiling with Na_2CO_3 . . .	
equals "free ammonia"	
expelled on boiling with alk. permang.	
equals "albuminoid ammonia" . . .	
as nitrate	
as nitrite	
Hardness	
Oxygen consumed (by permanganate treatment) .	

After discussion of the report it was voted that it be printed and a copy be sent to each member of the section, and that it be referred back to the same committee for further consideration in the light of such criticisms and suggestions as may be received from others, to the end that in the form finally approved it may have the widest possible adoption.

The committee therefore invites from all who may see this report and are interested in the subject, an expression of approval of the schemes proposed, or of disapproval, with the reasons for the same and suggestions for their amendment.

Communications may be sent to the chairman of the committee at Ithaca, N. Y.

The editor of the Journal of Analytical Chemistry has kindly offered to print and distribute the report.

G. C. CALDWELL.

SOME CAUSES OF ERROR IN BLANK ANALYSES.

BY J. B. MACKINTOSH.

IN making chemical investigations, it is quite usual to run a blank analysis, in order to apply a correction to our results for the impurities contained in the reagents and for those entering into solution from the apparatus used. As a rule however, it seems to be entirely overlooked that the conditions of the actual analysis are often quite different from those obtaining in the case of the blank. For instance, let us assume the case of a limestone which has been dissolved in just sufficient hydrochloric acid to form a neutral solution of calcium chloride; at this stage our blank analysis will be a strongly acid solution. If we now add to both enough ammonia to neutralize the amount of hydrochloric acid previously employed, we will have in our actual analysis a strongly ammoniacal solution, while in our blank there will be a neutral solution of ammonium chloride, and similar results will take place on the addition of every reagent. In such a case our blank analysis will give us only approximately correct results, for though any impurities existing in the chemicals will be detected, yet the impurities which are dissolved from our beakers by the solutions, will be quite different in the case quoted, and the errors due to this last source may far exceed those due to impurities contained in the chemicals used.

The particular case of blank analysis to which I desire to call attention, serves to illustrate the serious error into which chemists may be led by faith in the infallibility of books of reference, whose statements, copied from one another, gain in authority through force of iteration, even though, as some-

times is the case, the original statement be erroneous.

Several years ago I had occasion to analyse a large number of samples of metallic copper and alloys of copper, and for the determination of arsenic I decided to use the method of distillation with ferric chloride and hydrochloric acid recommended in Crooke's Select Methods.* In that work the statement is made that the ferric chloride employed may be freed from all traces of arsenic by one or two evaporations to dryness with hydrochloric acid, whereby the arsenic will all be volatilized as chloride. In following these directions I collected the distillates, thus making a blank analysis in all respects similar to the actual analyses performed later. When the distillates were tested for arsenic they were found to be perfectly free from that element, from whence the deduction was drawn that the reagents employed were pure. If the statement mentioned above was correct, then this deduction was justified by the facts observed. I noticed however that all the samples of copper I had, no matter of what quality, invariably caused the appearance of large quantities of arsenic in the distillates, and on repeating the experiment with the substitution of some charcoal for the copper, I likewise obtained arsenic in the distillate, and since the charcoal could not be suspected of being the source of the arsenic found, it was definitely traced to the ferric chloride, which by a blank analysis would have been pronounced pure. In this case the omission of the copper in the blank analysis was also the omission of a necessary reagent, without which or some substitute, the reaction would not take place. In fact, it is not until the arsenic is reduced to arsenious chloride that it will distill off, any arsenic in the higher form of oxidation not being volatile under these circumstances.

Here is a striking instance of the unreliability of blank analyses, unless all the circumstances be thoroughly comprehended and taken into account, and other instances of similar nature could readily be adduced.

*First Edition p. 266. Second Edition p. 431.

Lehigh University, South Bethlehem, Pa.

ABSTRACTS.

APPARATUS AND REAGENTS.

Purification of Sulphuretted Hydrogen from Arsenic.—O. Jacobsen, Ber. d. deut. chem. Ges. 20, 1999. The sulphuretted hydrogen obtained from sulphide of iron and sulphuric acid may be entirely freed from arseniuretted hydrogen by passing the partly dried gas over solid iodine.

Detection of Nitrogen Compounds in Sulphuric Acid containing Selenium.—G. Lunge, Ber. d. deut. chem. Ges. 20, 2031. The only reaction which gives trustworthy results with sulphuric acid containing selenium is the Brucine reaction. Diphenylamine gives a blue color with sulphuric acid containing selenious acid even if no nitrogen compounds are present. Ferrous sulphate gives a dark ring with such acid exactly like the nitric acid ring.

Indigo is decolorized by such acid just as if nitric acid were present.

Adjustable Thermometers.—A. Haddow, Jour. Soc. Chem. Ind. 6, 130. The thermometer tubing is carefully selected of even diameter, so that the distance between 10° upon any part of the scale is nearly the same. The thermometer is fastened to a separate piece sliding in the scale.

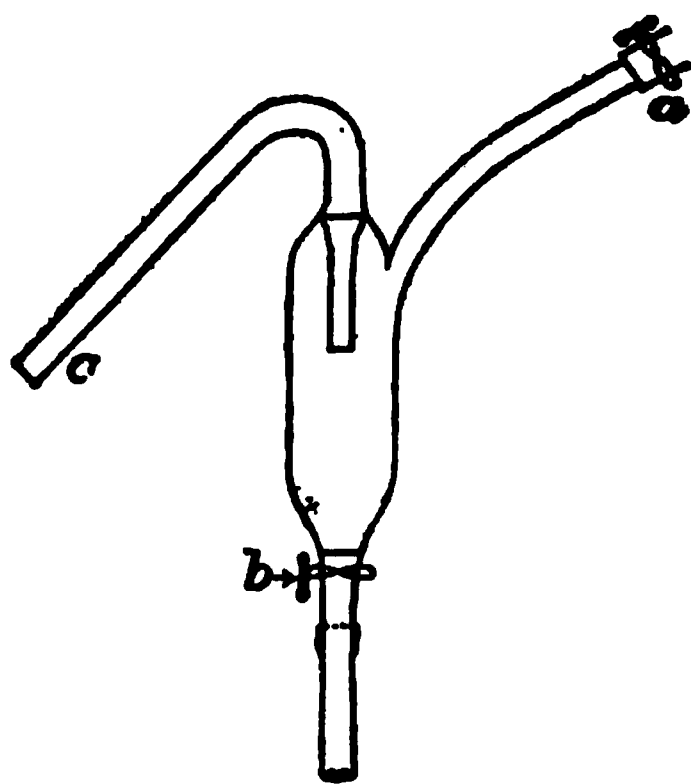
A Hot Blast Oxyhydrogen Furnace.—H. N. Warren, Chem. News 56, 29. An ordinary injector furnace is lined with about two inches of a paste composed of slaked lime and baryta. The lining is afterwards heated to whiteness to render it compact. The hot blast is made by surrounding spiral tubes one-half inch in diameter and seven feet long with an iron casing pierced with numerous draught holes and provided with a chimney to increase the draught. The fuel is a mixture of coke and charcoal. The oxygen tube is made of fire clay and the tube for coal gas of iron coated with boracic acid. The

ends of these tubes are connected with the furnace blowpipe when in use. A temperature as high as that of the electrical furnace can be obtained in this way.

Improved Filtering Funnels.—B. Nickels, Jour. Soc. Chem. Ind, 6, 327. A double funnel, the inner attached to the outer by means of suitable ribs or projections placed at intervals. The inner funnel is without a stem and is perforated. In another form the space between the two funnels at the top is closed, with a stopper for the admission of air and for cleaning purposes. The author claims that these funnels filter more rapidly, and that the back of a filter can be washed by introducing water into the annular space and closing the neck. Dialysis may be easily and conveniently carried on with this funnel. The filter for this purpose is made of parchment paper, the liquid to be dialysed poured in and water introduced into the annular space.

The Evolution of Sulphur Dioxide and Oxygen with Kipp's Apparatus.—G. Neumann, Ber. d. deut. chem. Ges. 20, 1584, uses Winkler's plan,* for evolving sulphur dioxide and oxygen. For the former the cubes are made of three parts calcium sulphite and one part gypsum and for the latter of two parts barium dioxide, one part manganese dioxide and one part gypsum.

A New Siphon.—Ad. Jolles, Rep. anal. Chem. 7, 151. C is placed in the liquid. By closing *b* and applying suction at *a* the siphon is filled, and is set in operation by closing *a* and opening *b*.



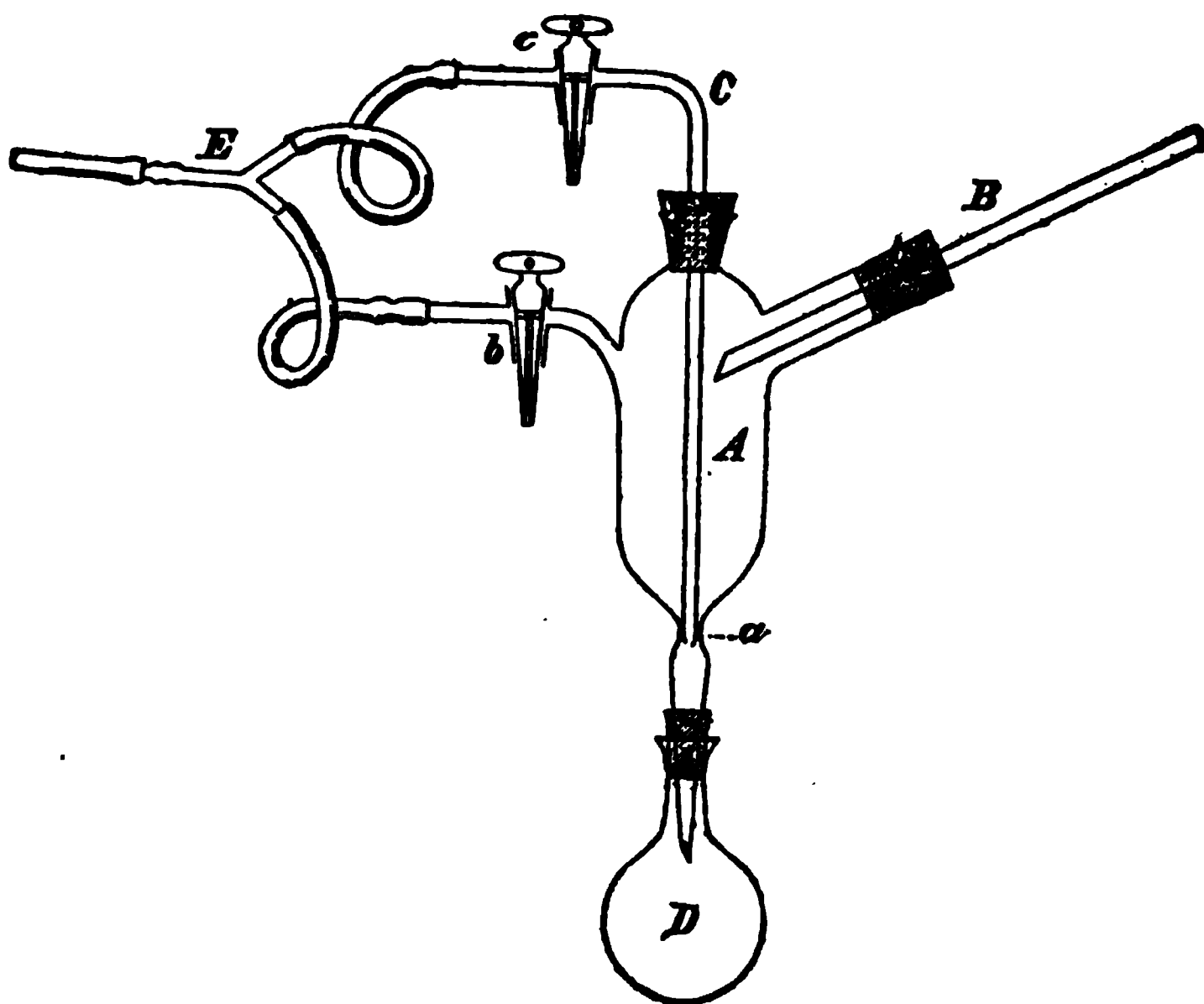
Apparatus for Determining the Specific Gravity of Solids.—Ding. poly. Journ. 263, 30. The apparatus consists of a specific gravity bottle the stopper of which is drawn out into a capillary tube terminating above

* See this Journal 1, 315 and 316.

in a small funnel. The bottle is also drawn out below, and connected, by means of rubber tube, with a 10 c. c. burette. The burette and bottle are then fastened in clamps so that they can be raised and lowered at will.

The bottle is now filled with water and lowered until the water rises to a mark on the capillary tube, and the level of the water in the burette read off. The bottle is raised, the solid dropped in, lowered until the water again reaches the mark on the capillary tube and the volume of liquid in the burette again read off. The difference in volume between the two readings is equal to the volume of the solid which divided into the weight gives the sp. gr. The method is very rapid and gives results within one-fourth per cent. of the truth.

Apparatus for Fractional Distillation under Diminished Pressure.—V. Meyer, Ber. d. deut. chem. Ges. 20, 1833. *B* is the lower end of the condenser. The tube *C* is ground into *A* at *a*. *E* leads to the pump. When the distillation is begun

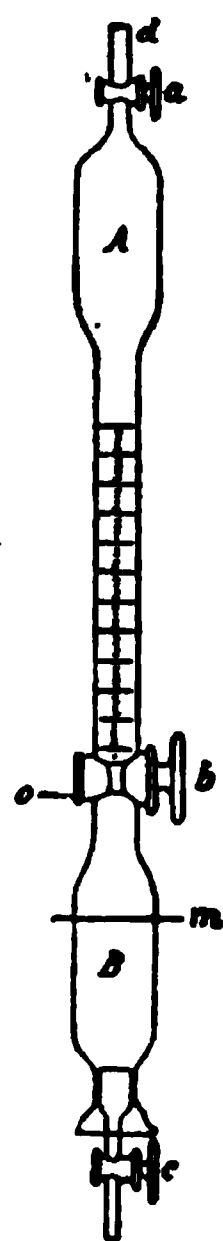


C is raised until the bulb *D* is filled, then lowered until *D* is emptied. While *D* is being emptied communication with the

pump is kept up through *b*, *c* being closed. *D* can be taken off more easily if air is first admitted through the three-way cock *c* and tube *C*.

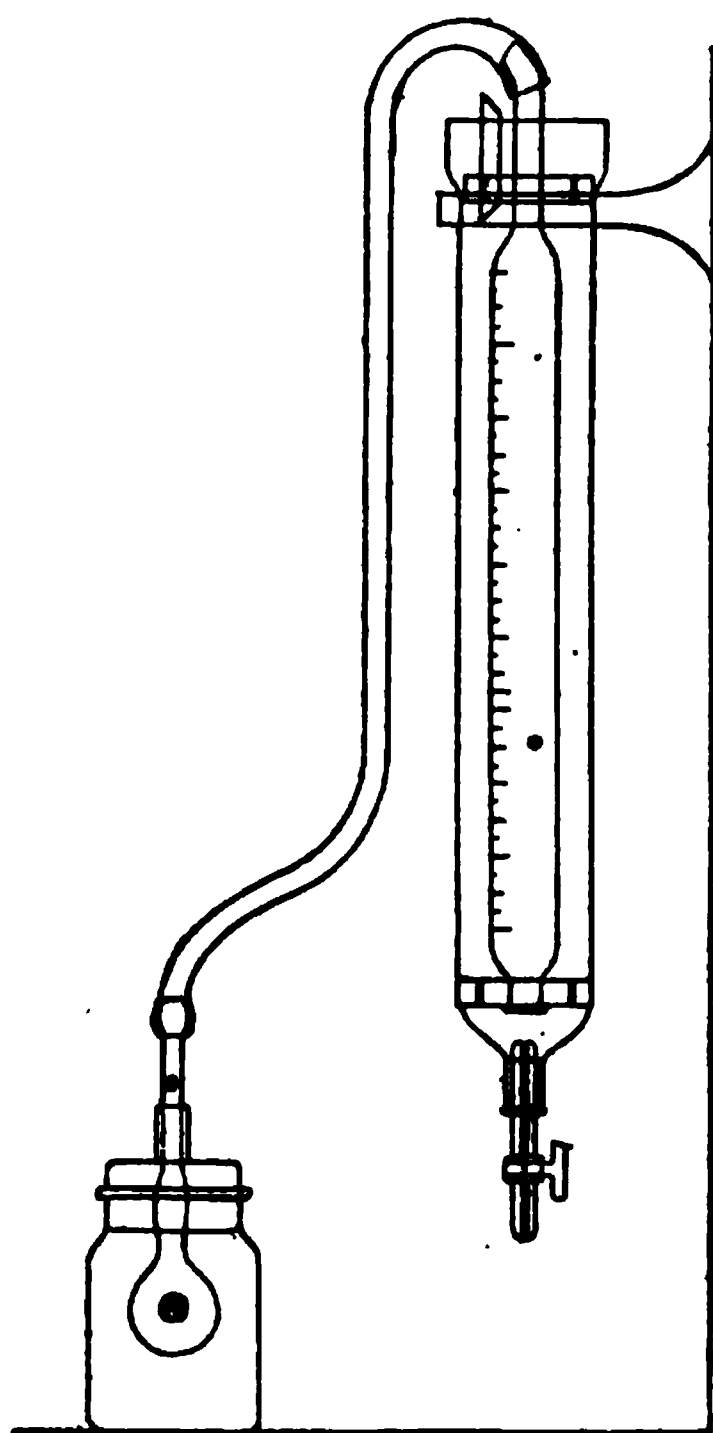
A Vacuum Drying Apparatus is described by P. Schoop, Zeit. f. Chem. Ind. 1887, 2, 33. It consists of a wide glass tube, 150 cm. long and 50 mm. wide, drawn out to a short tube at one end, which is connected by a ground joint with a small retort, with short neck, containing sulphuric acid. A stopper terminating in a tube is ground over the other end and the tube is connected with the air pump. In use, the large tube is passed through a water bath, both ends projecting, and the sulphuric acid bulb is attached to one end and the stopper to the other.

A New Gas Burette. — B. Franke, Jour. prak. Chem. 35, 260. The burette consists of the measuring chamber *A* and the reagent chamber *B*, connected by a stop-cock with wide bore. The burette is filled, either by passing the gas through it for some time or by filling the burette with water and allowing gas to pass in at *d* while water runs out at *c*. As soon as the gas has reached the point *m*, *a* and *c* are closed and the burette placed in a vessel of water. *c* is opened and the burette raised or lowered so that the water has the same level in the burette and containing vessel. *b* is then closed and we have a definite volume (100 c. c.) of gas in *A*. If an estimation of CO₂ is to be made the vessel *B* is filled with caustic potash solution, *c* closed, *b* opened and the liquid run into *A*. After absorption is complete the tube is placed in an upright position and when the liquid has filled *B*, *b* is closed and the reagent is washed out, the vessel *B* filled with water, the burette placed in a vessel of water, *b* opened, the water brought to the same level within and without and the volume of gas remaining read off.



If oxygen and carbon monoxide are to be estimated in the same sample the water remaining in the tube *A* is removed by

applying suction at *c* and closing *b* as soon as the surface of the water reaches that point, then the appropriate reagent is poured into *B* and the operation carried on as before.



Apparatus for Estimating the Carbon Dioxide in Carbonates.—R. Bauer, Jour. prak. Chem. 35, 86. An improvement on the apparatus previously described by the author. (Ibid. 29, 490). The inner tube on the right of the figure is for measuring the gas given off. The outer tube contains water which can be drawn off by the stop-cock below. The small flask contains the carbonate and the bulb tube the acid. This bulb has an opening about half way up the side, so that by inclining the flask the acid runs out on the carbonate. It also has a small side opening in the tube just above the cork, for adjusting the level of the water in the measuring tube before

beginning the experiment. When this adjustment is made the tube is pushed down until the opening comes within the rubber tube attached to the cork. The apparatus must be carefully tested for leaks, and no more than the necessary amount of acid must be used.

A New Apparatus for Distillation has been described by M. U. Gayon (Ann. Chim. Phys. [6] 11, 555.) The apparatus is quite complicated and was devised by the author for the separation of alcohol at one operation from fermented liquids. The reader should consult the original article.

A Modification of the Ferric Chloride Cell.—Thos. Moore, Chem. News 56, 64, proposes to add potassium chlorate to the

ferric chloride cell instead of bromine as proposed by Warren. (This Journal, 1, 183).

Apparatus for Obtaining a Constant Supply of Gas.—Chr. Sleenbuch, Jour. prak. Chem. 35, 364. *a* contains the substance to be acted upon by the acid, (marble, manganese dioxide, etc.) closed below by a glass plate perforated with holes. A wash bottle is shown on the left. This is connected with a rubber tube and pinch-cock not shown in the figure. After *a* has been filled with the material to be used the acid is poured into *b* until the Woulff flask is filled and the reservoir partly so. The air contained in the Woulff bottle passes out through the small tube inside *d*. *c* is a siphon for drawing off the acid after it has become saturated. As the acid becomes saturated in *a* it falls to the bottom of the Woulff flask through *d*, fresh acid rising through the inner tube to take its place. With 12 per cent. hydrochloric acid and ferrous sulphide the author obtained 26, 15, 17, 13, 15, 15 and 10 gms. H_2S in eight consecutive hours. A steady stream of chlorine may be obtained from HCl and 90 per cent. MnO_2 by coiling lead pipe around *a* and passing steam through it.

A New Pyrometer.—E. H. Keiser, Amer. Chem. Jour. 9, 296. A bulb tube of a capacity of 100 c. c. with capillary stem connected by a thick rubber tube to the top of a graduated tube immersed in water. The bulb tube is introduced into the heated substance and the temperature ascertained from the increase of volume of the air in the graduated tube using the formula

$$t_1 = t + \frac{V}{C - \frac{V}{273+t}}$$

in which t_1 = the desired temperature in centigrade degrees.

t = temperature of the room and eudiometer.

V = volume of air driven over.

C = a constant for any given temperature t .

The value of C depends upon the capacity of the bulb and upon the coefficients of expansion of air and the material of the bulb at the temperature t . It may be determined by placing the bulb in steam or any other vapor of known temperature and measuring the volume of gas driven over. Then by substituting the known quantities in the formula the equation may be solved for C .

Marking Weighed Porcelain Vessels.—B. Blount, Chem. News, 56, 66. The letters are written with a diamond, smeared with platinic chloride solution and wiped dry, then the vessel ignited; the letters stand out marked in metallic platinum.

The Influence of Minute Quantities of Sulphuric Acid on the Action of Water on Lead.—W. C. Williams, Jour. Soc. Chem. Ind. 6, 111. It was found that small quantities of free sulphuric acid in water or dilute saline solutions increase the action on lead in a marked degree. The amount of lead in solution increased steadily up to a certain point (24–48 hours usually) when the solution becomes turbid and the dissolved lead decreases in amount. The rapidity of solution as well as the amount dissolved is greatly influenced by the condition of the lead acted on and by the temperature.

Determination of the Vapor Density of High Boiling Substances under Diminished Pressure.—C. Schall, Ber. d. deut. chem. Ges. 20, 1435, 1827, 2127. The original papers must be consulted.

A Portable Apparatus for the Estimation of Carbon Dioxide in Air is described and figured by Petterson and Palmqvist, Ber. d. deut. chem. Ges. 20, 2129. The reader is referred to the original paper.

Vapor Density Apparatus.—D. S. Macnair, Chem. News, 55, 289. A modification of Hofmann's apparatus. For the inner mercury tube of Hofmann's apparatus a siphon barome-

ter tube is substituted. The ends of the siphon barometer tube are made larger than the middle portion.

Scheme for Qualitative Blowpipe Analysis.—A. J. Moses, *School of Mines Quarterly* 8, 359.

Complete Apparatus for Titration of Acids.—F. Larssen, *Zeit. anal. Chem.* 26, 333. The large bottle for holding stock solution is fastened to a heavy block of wood which forms the base of the apparatus. Around the stock bottle near the base is fastened a metal ring and to this are attached on one side two open-top metal cylinders for holding, the one a bottle of litmus solution, the other a bottle containing test papers. On the opposite side of this ring is attached a metal ring for supporting an evaporating dish. Over the dish the burette is held, near its base, by a clamp fastened around the neck of the bottle. The upper end of the burette is steadied by the tube for filling it which passes into the stock bottle. A side tube near the top of the burette allows suction to be applied for drawing the stock solution into the burette. Through the cork of the stock bottle passes another tube for purifying the air passing in, and to this tube are fastened supports for holding pipettes.

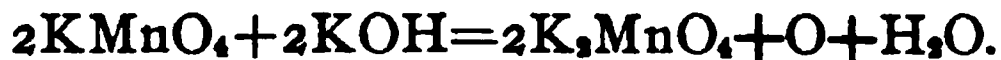
[The apparatus seems entirely too complex in arrangement. The parts would probably get out of adjustment and encourage profanity.—E. H.]

Gas Evolution Apparatus for Gas Analysis.—A. Ehrenberg, *Zeit. anal. Chem.* 26, 226. The apparatus is made by cutting off the top of a wide mouthed bottle so as to form a bell jar with open top. The mouth is closed with a plate of hard rubber perforated with a hole, through which passes a tube with stop-cock. The bell jar is then inverted and fastened in an iron ring which slides up and down upon the rod of a heavy retort stand. The wide (now the upper) end of the bell jar is now closed with another plate of hard rubber having three perforations. Two of these are for the gas tubes *a* and *b*, and the third for a short glass tube closed above with a cork and intended for pouring in the acid. The

tubes *a* and *b* have the shape of the inner tube of the Bunsen gas generator, except that the bottom of the tube is removed. The tube *a* contains two electrodes which are connected with wires passing through the bottom hard rubber plate and fastened to binding posts. *b* contains only one electrode which is also fastened in the same way to another binding post. In this way from *a* either pure hydrogen or a mixture of two volumes hydrogen and one of oxygen, and from *b* pure oxygen can be obtained. The apparatus is filled with acid through the third small tube in the upper plate and the upper parts of the evolution tubes are filled by removing the stoppered delivery tubes.

Potassium Manganate and its Applications in Analytical Chemistry.—Ad. Jolles, Rep. anal Chem. 7, 485. A solution of pure potassium manganate differs in behavior from an alkaline solution of potassium permanganate.

The potassium manganate used was prepared as follows: Pure potassium hydroxide is placed in a crucible, a little water added and heat applied, adding gradually the calculated amount of pulverized potassium permanganate, according to the reaction.



The mass is stirred and heated for about two hours to low redness. The crucible is now cooled and dropped into a glass bottle closed with ground stopper to keep it from contact with the air. A solution of potassium manganate differs from an alkaline permanganate solution as follows:

(1) Alkaline manganate solution forms with certain metallic oxides compounds of definite composition which settle rapidly; this is not the case with alkaline permanganate solution. Here precipitates of indefinite composition are formed which do not settle readily, but adhere to the walls of the containing vessel.

(2) Alkaline manganate solution has very powerful oxidizing properties, so that certain substances are oxidized readily and uniformly at the ordinary temperature. With alkaline permanganate an excess of the reagent and heat, are necessary to complete the oxidation.

(3) The end reaction with alkaline manganate is easy to determine and is shown by the loss of green color—the solution becomes colorless. Alkaline permanganate solution does not keep well but constantly deposits a mixture of MnO_2 and Mn_2O_3 . When used as an oxidizing agent the end reaction is slow and is accompanied by changes in the color of the solution which completely mask it.

It is probable that the alkaline manganate acts first upon water oxidizing it to H_2O_2 which then oxidizes the substance in solution. The author has been led to this conclusion, because a crystal of manganate has no action on alcohol until a little water is added. It may be, however, that in this case the water is necessary only as a solvent for the K_2MnO_4 .

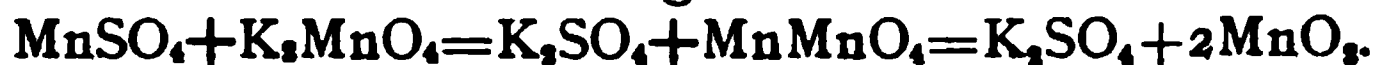
In certain cases the manganate acts as a reducing agent; lead dioxide, for example, is reduced to oxide by it with the evolution of oxygen.

When an alkaline manganate solution is added to alcohol, after several changes of color the solution becomes colorless and a yellowish brown deposit is formed. This deposit is potassium manganite, K_2MnO_3 , and the solution contains aldehyde.



This manganite is easily reduced in presence of an excess of alcohol, MnO_2 forming.

Manganese may be estimated by means of the alkaline manganate solution as follows: A measured amount of a slightly alkaline solution of the manganate, of known strength, is placed in a flask and the solution in which the manganese is to be determined is run in from a burette until the manganate solution loses its green color. There is no necessity for the addition of a zink salt, and the precipitate consists of manganese dioxide free from manganous oxide.



Cobalt may be determined in the same way. The precipitate formed has the composition CoMnO_3 .

Sulphuretted Hydrogen and Sulphides when added to alka-

line manganate solution are oxidized to sulphites and sulphates, and MnO_2 precipitates.

Sulphites are completely oxidized to sulphates.

The action of the solution upon the organic acids, especially tartaric, malic and citric, will be examined and reported upon.

Improvements in Methods of Chemical Calculations.—E. A. Uehling, *The Stevens Indicator*, 4, 142. The standard method of calculating the results of chemical analysis by proportions is too tedious. The use of tables greatly facilitates the work and reduces the liability to error but still has the drawback of being more or less cumbersome.

If, instead of weighing out an even number of grammes, *"we weigh out a number of grammes equal to the per cent. of the element to be determined in the precipitate to be weighed, the weight of the precipitate is the per cent. of the element sought in the substance analyzed."*

Should the per cent. of the element in the final precipitate give too large a quantity, take one-half, one-fifth, one-tenth or one-hundreth, and then multiply the weight of the final precipitate by 2, 5, 10 or 100, as the case may require.

For convenience, the required weight of the substance to be analyzed for the element to be determined and the proper multiplier may be written on a card and placed in the balance. Thus :

For phosphorus weighed as $\text{Mg}_2\text{P}_2\text{O}_7$, if we take

$W=9.303$ grms.; then $w \times 3 =$ per cent.

$W=5.5854$ " " $w \times 5 =$ "

$W=2.727$ " " $w \times 10 =$ "

For sulphur weighed as Ba SO_4 , if we take

$W=13.73$ grms.; then $w \times 0 =$ per cent.

$W=6.865$ " " $w \times 2 =$ "

$W=2.75$ " " $w \times 5 =$ "

For Silicon weighed as Si O_2 , if we take

$W=9.3333$ grms.; then $w \times 5 =$ per cent.

$W=4.6667$ " " $w \times 10 =$ "

$W=0.4667$ " " $w \times 100 =$ "

In general if

W = weight of the substance taken for analysis.

w = " " final precipitate.

P = Per cent. of the element sought.

n = a convenient multiplier.

Then $W = \frac{P}{n}$ and $P = wn$.

In laboratories where a great number of determinations of the same element occur daily, the operation of weighing may be still further facilitated by having special weights prepared for each of the elements which are of frequent occurrence. Thus for silicon have a weight of exactly 0.4667 grms. marked Si. For phosphorus one weighing 2.727 grms. marked P. For sulphur one weighing 6.865 grms. marked S, etc.

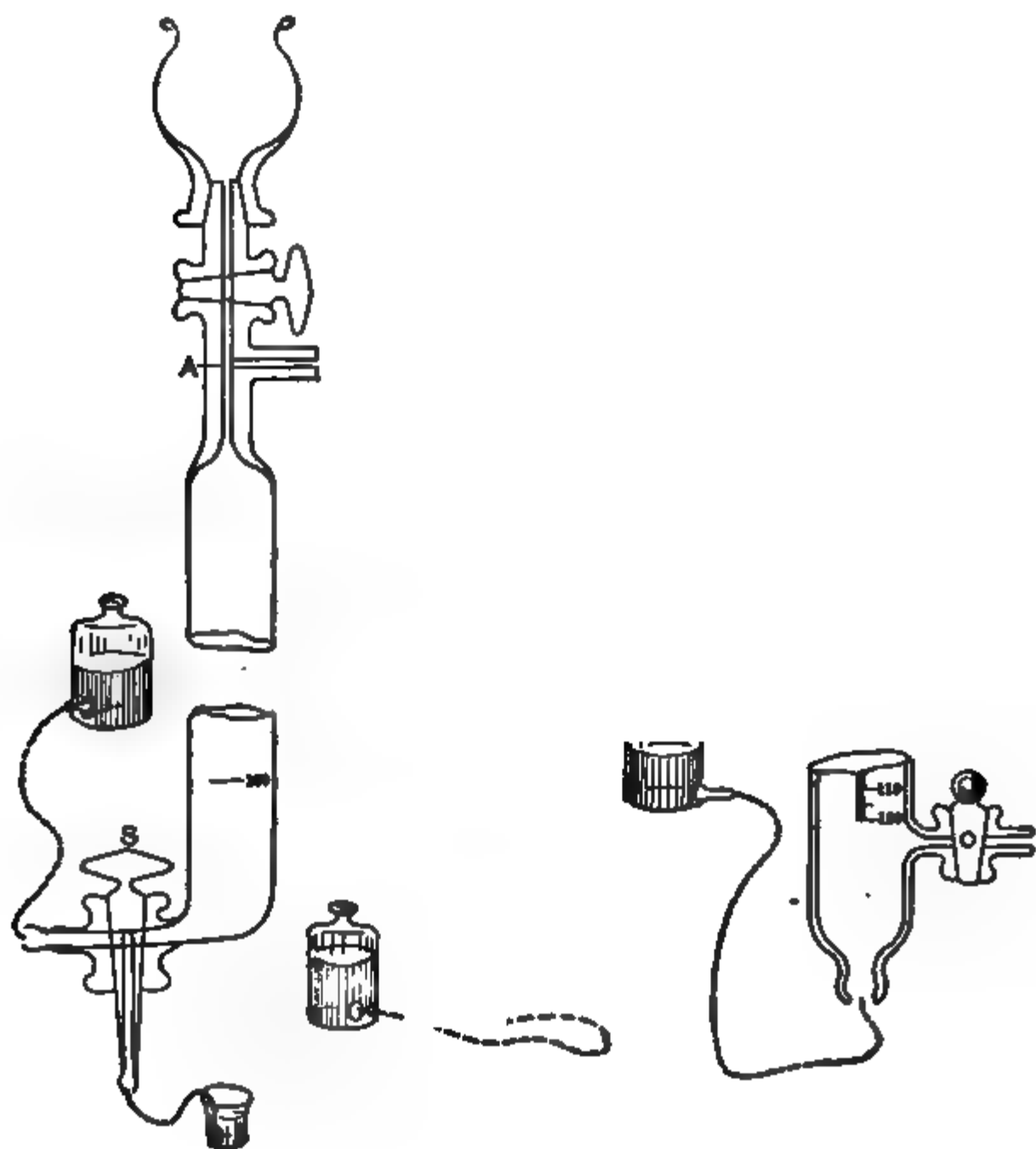
A. L. COLBY.

An Improved Form of Elliott's Gas Apparatus.—J. B. Mackintosh, Amer. Chem. Jour. 9, 294. "In the ordinary form of this apparatus as described by Elliott,* the transfer of the residual gases from the absorption apparatus to the explosion burette is attended with some difficulty and with the liability of accidentally introducing some air during the operation unless great care be taken. In order to obviate these troubles and, incidentally, also to diminish the number of loose pieces, I have devised the simple modification shown in the illustration. The essential feature is the three-way T-stopcock on the measuring burette, whereby connection may be made between any two of the burettes, to the complete isolation of the other. Another time-saving device is in the fixing of the zero points of the graduations. In the measuring and explosion burettes the zero point O is taken at that point where the capillary tube expands into the burette, and where the water will naturally remain when the excess drains to the bottom of the burette. This renders the adjustment to zero an automatic one, with no sacrifice of accuracy. The absorption tube has a single graduation at 100 c. c. measured from the point A . In filling this tube with

*School of Mines Quarterly 3, 16, and 4, 322; and Chemical News, October, '83.

gas to the mark, a small quantity remains in the portion of the tube above *A*, but this may be removed by first closing the lower stopcock *S* and then forcing water out of one of the other burettes. This slightly compresses the gas in the absorption tube, and at the same time expels the excess, so that we then have exactly 100 c. c. at the atmospheric pressure.

In transferring gas to the explosion burette from the measuring tube, the portion remaining in the capillary tube and in the ways of the T-stopcock is removed by passing water



from the absorption tube, preferably by letting it flow in from the funnel. The T-stopcock being then turned so as to connect the explosion and absorption tubes, the gas remaining in the measuring tube is perfectly isolated, and none of it has been lost during the transfer. We are now ready to introduce oxygen and air for the explosion, which may be done either as Elliott directs, through the lower stopcock of the explosion burette, or through the funnel of the absorption tube, or both.

In case we have not a store of oxygen under pressure for use, I have found that a very convenient source of this indispensable reagent is available in the reaction of peroxide of hydrogen on acidified solution of potassium permanganate. We can thus manufacture in the absorption tube as much pure oxygen as we need, by first running in some permanganate, then the peroxide of hydrogen, and then more permanganate, until we have added enough to decompose all the peroxide taken. We then wash the permanganate out of the funnel, etc., with water, pass as much oxygen as we need into the explosion burette, empty the capillary tube of oxygen as before by letting water run in from the funnel, and, finally, empty and wash out the absorption tube and make it in readiness for the absorption of the carbonic acid resulting from explosion. Air may now be introduced in sufficient quantity, and after mixing the gases by removing and inclining the burette, the explosion may be made, the contraction noted, the gas transferred to the absorption burette, and the carbonic acid absorbed, and, finally, retransferred to the explosion burette and the residual gas measured."

INORGANIC ANALYSIS.

On the Determination of Arsenic as the Pentasulphide, by L. W. McCay, Amer. Chem. Jour. 9, 174. Some time ago L. W. McCay showed that arsenic could be rapidly and completely precipitated as the pentasulphide by heating a strongly acidified solution of an alkaline arseniate, saturated

with sulphuretted hydrogen, in a hermetically sealed bottle and in a boiling water bath for one hour. (Chemical News 54, 287.)

This device for precipitating arsenic he has now made the basis of a method for estimating the element. McCay gives two modes of procedure. The second he recommends as most convenient.

1. The solution of arsenic acid which should equal about 150 c. c. is strongly acidified with hydrochloric acid, brought into a little bottle provided with a tightly fitting ground glass stopper and capable of holding when filled to the neck 200 c. c., and treated with sulphuretted hydrogen gas until a faint but distinct opalescence makes its appearance. The bottle is then closed, the stopper firmly tied down with a piece of cord and the whole placed in the boiling water bath and here kept for one hour. At the end of the hour the bottle is removed from the bath, allowed to cool and violently shaken so as to cause the pentasulphide to settle rapidly leaving the supernatant liquid clear. Its contents are filtered on a weighed filter paper, dried at 110° C and the precipitate is washed with water, until the filtrate gives no reaction for chlorine, and then, in regular order, six times with alcohol, four times with bisulphide of carbon and again four times with alcohol. The pump will be found very convenient. The drying is done at 110° C. and to constant weight. Two hours invariably prove sufficient. From a number of test analyses we select the following two :

<i>Taken.</i>	<i>Calculated.</i>	<i>Found.</i>
I. 20 c.c. $\frac{n}{10}$ H_3AsO_4	0.1550 gram As_2S_5 =0.0750 gram As.	0.1555 gram As_2S_5 =0.0752 gram As.
II. 50 c.c. $\frac{n}{10}$ H_3AsO_4	0.3875 gram As_2S_5 =0.1875 gram As.	0.3875 gram As_2S_5 =0.1875 gram As.

To avoid the use of alcohol and bisulphide of carbon in washing the precipitate, the following mode of procedure is recommended :

2. The solution, after having been brought into the bottle

and acidified with hydrochloric acid, is diluted with freshly boiled water until the bottle is nearly full, and then saturated with sulphuretted hydrogen. By so doing almost all the air is expelled from the bottle, and a subsequent separation of sulphur from the sulphuretted hydrogen by the action of any free oxygen rendered next to impossible. The rest of the process is then conducted exactly as has been already described. The sulphide is washed with water until the filtrate is free from chlorine. It will be found well, in order to hasten the subsequent drying of the precipitate, to replace the water adhering to the same by running a small quantity of alcohol through the filter. This, however, is not necessary.

The test analyses given are fully as satisfactory as those obtained by the first method. The following three, taken at random, will exhibit the degree of accuracy of this mode of procedure :

<i>Taken.</i>	<i>Calculated.</i>	<i>Found.</i>
I. 25 c. c. standard } H ₂ KAsO ₄ }	0.2670 gram As ₂ S ₃ =0.1292 gram As.	0.2675 gram As ₂ S ₃ =0.1294 gram As.
II. 50 c. c. standard } H ₂ KAsO ₄ }	0.5340 gram As ₂ S ₃ =0.2584 gram As.	0.5350 gram As ₂ S ₃ =0.2588 gram As.
III. 50 c. c. stand. } H ₂ KAsO ₄ }	0.5340 gram As ₂ S ₃ =0.2584 gram As.	0.5335 gram As ₂ S ₃ =0.2582 gram As.

The process is essentially a modification of the Bunsen method for determining arsenic. It is, however, a great improvement upon the Bunsen method for the following reasons :
 1. It is remarkably rapid. 2. The quantity of sulphuretted hydrogen necessary for precipitation is reduced to a minimum. 3. No alcohol nor bisulphide of carbon is necessary for washing. 4. The pentasulphide does not stick to the sides of the bottle, but separates out in such a state that every trace can be removed without even the aid of a feather.

New Methods of Estimating Arsenic in Pyrites, Etc.—
 John Clark, Jour. Soc. Chem. Ind. 6, 352.

Precipitation Process.—About 3 gms. of the finely ground pyrites is mixed with 12 gms. of a mixture of equal parts of

magnesia and sodium hydrate in a platinum crucible and the mixture heated for 10 minutes over a low Bunsen's flame. The mixture shrinks but does not liquefy. The mass is extracted with water, filtered, the filtrate acidified with HCl and H_2S passed through to ensure the precipitation of all the arsenic. The precipitate is filtered, the sulphide of arsenic dissolved out with ammonia, the filtrate evaporated to dryness, oxidized with nitric acid and the arsenic acid estimated, either volumetrically by Volhard's process or by precipitation as magnesium ammonium arsenate. On account of the large amount of pyrites which can be taken, very small quantities of arsenic can be detected by this process and very accurate results obtained.

Distillation Process.—1.7 gms. finely powdered pyrites is heated in a platinum crucible with six times its weight of the above mixture of sodium hydroxide and magnesia for an hour. The contents of the crucible are then broken up with a spatula, transferred to a flask, moistened with a little water and 70 c. c. strong HCl added. The crucible is also washed out with strong HCl which is poured into the flask; the flask is then heated until there is no further action. The flask is now fitted with a cork bored with two holes, in one of which a funnel tube passes and through the other the end of a condenser. A considerable excess of a solution of cuprous chloride in HCl is then added through the funnel tube and the liquid distilled for an hour into water. More HCl is then introduced and the distillation continued for a half hour. All the arsenic will be found in the distillate, but it is advisable to distill a third time and test the distillate for arsenic. The arsenic is then precipitated as sulphide in the usual way.

Two samples of arsenious acid, weighing 3.96 grains each, gave 3.94 and 3.90 grains respectively. An arseniate of soda, which yielded 50.03 per cent. arsenic acid by precipitation in the ordinary way, gave 50.15, 50.33 and 50.00 per cent. The author gives numerous other test analyses giving equally good results.

On the Determination of Sulphur in Pyrites.—J. W.

Westmoreland, Jour. Soc. Chem. Ind. **6**, 84. Must be read in full.

On the Estimation of Sulphur in Pyrites.—G. Lunge, Jour. Soc. Chem. Ind. **6**, 96. The method proposed by Lunge having been attacked by J. C. Welch (Analyst, Nov. 1886), the author defends his process.

Determination of Sulphites in Presence of Thiosulphates and Sulphates.—Griffin & Little, Chem. News, **56**, 34. (See this Journal, **1**, 323.) "The sulphurous acid left in the solution is exactly one-half of the total amount present as bisulphate in the original solution only in special cases, since, allowing a little time for the reactions to become complete, the amount of sulphurous acid in solution reduces to a constant quantity for a given temperature, viz., about 0.15 per cent. at the ordinary temperature. This holds true for magnesium as well as alkaline bisulphites."

The sulphurous acid remains in solution as barium bisulphite and may be estimated either with NaOH or with iodine. If a solution containing sulphites and bisulphites is treated with lead acetate equivalent to the sulphur acids present free acetic acid is left in solution equivalent to just half the sulphurous acid present as bisulphite; and it may be determined with alkali.

The Separation and Estimation of Phosphoric and Tungstic Acids.—Fr. Kehrman, Ber. d. deut. chem. Ges. **20**, 1813. All orthophosphotungstic acids are decomposed by one-half hour boiling with caustic soda into bibasic tungstate and tribasic phosphate. If ammonium chloride is now added, in quantity sufficient to allow all the alkali to combine with chlorine, the phosphoric acid may be completely precipitated by means of magnesia mixture, free from tungstic acid. The precipitate is washed with dilute ammonia, containing ammonium nitrate, dissolved in nitric acid and precipitated with molybdic acid solution to free it from a little iron and alumina; finally, it is converted again into the magnesium compound in the usual way. In the filtrate from the first

precipitation of the phosphoric acid the tungstic acid is determined by evaporating to dryness—evaporating the residue four times with concentrated hydrochloric acid—washing with water containing a little nitric acid and ammonium nitrate and igniting at a dark red heat.

Estimation of Phosphoric Acid in Thomas' Slag.—G. Loges. Rep. anal. Chem. 7, 85. 10 gms. of the slag is treated with sulphuric acid (1 acid to 1 water) and then 50 c. c. concentrated sulphuric acid added. The mass is then heated on a sand bath till white fumes are given off. After cooling, the mass is treated with water, made up to a liter, the solution filtered and the phosphoric acid determined in 50 c. c. by precipitation with molybdic acid solution. The results obtained are slightly higher than by the hydrochloric acid method. The method is to be preferred because tedious evaporations to dryness are unnecessary.

Estimation of Caustic Soda in Soda Ash.—R. Williams, Jour. Soc. Chem. Ind. 6, 346, uses the following method: "A weighed quantity of ash is treated with strong alcohol in a stoppered flask, frequently shaken and allowed to stand over night; the undissolved carbonate is filtered off and washed with strong alcohol until a drop gives no alkaline reaction; the filtrate and washings are then titrated with normal acid."

Peter Hart, Ibid. 347, uses the following method: "50 grains of the sample is dissolved and made up to $\frac{1}{2}$ to $\frac{3}{4}$ pint, a little phenolphthalein added and the test acid (1 decem. = 0.5 Na₂O) slowly run in until the color disappears. At this point all the caustic soda and *one-half* the soda existing as carbonate has been neutralized, the number of measures—say thirty—is noted. To the same solution (the soda in which now exists as bicarbonate), a little metyhlorange is added, and the addition of acid from the same burette continued, until the usual color indicating neutrality occurs—say the burette now reads 50. Then $50 - 30 = 20$ as bicarbonate which originally existed as monocarbonate in the sample. This, therefore, must be doubled = 40. This, deducted from the total number 50, leaves 10 existing in original sample as caustic soda."

Examination of Soda Mother Liquors.—Kalmann and Spüller, Ding. Poly. Jour. 264, 456. (1) In a measured volume the total alkalinity is determined with normal acid and methyl orange. The acid used corresponds to sodium sulphide + sodium hydroxide + half the sodium sulphite.

(2) An equal volume is acidified with acetic acid, starch paste added and the solution titrated with $\frac{N}{10}$ iodine solution. This gives sodium sulphide + sodium sulphite + sodium thiosulphate.

(3) From double the volume used in (1) and (2) the sulphide is precipitated with alkaline zinc solution, made up to a definite volume, filtered and the filtrate acidified with acetic acid and titrated with $\frac{N}{10}$ iodine and starch paste. The result is sodium sulphite + thiosulphate.

(4) Three to four times the volume used in (1) and (2) is treated with BaCl_2 in excess, made up to definite volume with boiled water, filtered: *a* — one-third or one-fourth of the filtrate, is now titrated with normal acid. The acid used corresponds to sodium hydroxide + sodium sulphide. *b* — another third or fourth is acidified with acetic acid and titrated with $\frac{N}{10}$ iodine. This gives sodium sulphide + thiosulphate. The calculation is as follows:

$$\begin{array}{llllll}
 2-4b=A \text{ c. c. } \frac{N}{10} \text{ iodine solution corresponding to the } & \text{Na}_2\text{SO}_3 \\
 2-3=B \text{ c. c. } & \text{Na}_2\text{S} \\
 4b-(2-3)=C \text{ c. c. } & \text{Na}_2\text{S}_2\text{O}_3 \\
 4a-\frac{1}{10}B=D \text{ c. c. normal acid corresponding to the } & \text{NaOH} \\
 1-(4a+\frac{1}{20}A)=E \text{ c. c. } & \text{Na}_2\text{CO}_3
 \end{array}$$

A Delicate Test for Bismuth.—F. B. Stone, Jour. Soc. Chem. Ind. 6, 416. When potassium iodide is added to a solution of bismuth sulphate containing only a small amount of free sulphuric acid it produces a bright yellow color which can be used as the basis for a colorimetric process for the estimation of minute amounts of bismuth. The test is especially useful for detecting small amounts of bismuth in copper, for although a small quantity of bismuth is dissolved when ammonia and ammonium carbonate are added to a bismuth

solution this is not the case when a large amount of copper and also a small quantity of iron are present. 0.0001 gm. bismuth may be detected in 10 gms. copper. The precipitated bismuth carbonate is washed with a little dilute ammonia and ammonium carbonate until free from blue color, dissolved in a very small amount of dilute sulphuric acid, a few drops of potassium iodide added, and afterwards a few drops of sulphurous acid to remove the iodine set free by the ferric sulphate present. Trials of the method gave the following results:

<i>Bi₂O₃ Taken.</i>	<i>Found.</i>	<i>Taken.</i>	<i>Found.</i>
0.0001	0.00011	0.0004	0.00035
0.00015	0.00013	0.0007	0.00073
0.0002	0.00021	0.0010	0.00092

Volumetric Estimation of Cobalt in Presence of Nickel.—N. McCulloch, Chem. News, 56, 27. The author has examined the method of Fleischer and the modified method proposed by Donath. Fleischer's method is as follows: The acid solution of the two oxides is boiled with caustic soda and sodium hypochlorite and the oxides boiled in the same liquid with excess of bromine to ensure complete oxidation. The oxides are then dissolved in an excess of normal ferrous sulphate and the excess estimated by permanganate; this gives nickel plus cobalt. In a second portion the oxides obtained as above are boiled with a 3 per cent. solution of ammonia, which reduces the nickel to protoxide without affecting the cobalt. The mixed oxides are titrated with ferrous sulphate and permanganate; this gives the cobalt. The difference between the two gives the nickel.

In Donath's modification iodine is used instead of bromine, which oxidizes only the cobalt to sesquioxide, leaving the nickel as protoxide.

The author now finds that in a solution in which bromine is in excess an oxide is obtained having the composition $4\text{Co}_2\text{O}_3 + \text{CoO}_2$ and the results are too high; but where caustic soda is in excess, or where the solution contains free iodine or hydriodic acid, an oxide having approximately the composi-

tion $\text{Co}_{12}\text{O}_{19}$ is obtained and the results are too low. The results obtained confirm the work of Bayley (Chem. News, 39, 81).

The Analysis of Clay.—Meineke, Rep. anal. Chem. 7, 214.
Estimation of the Silica.—Two sources of error exist in the analysis of clay ; the first lies in the solubility of silica ; the second in that the silica as separated always contains more or less alumina. The author fuses .5 gm. clay with sodium bicarbonate and evaporates to dryness with acid on the water bath. The dried mass is then heated for some time to 300° on the sand bath and then to 150° in the air bath, until no more HCl can be smelled. The mass is treated with HCl, allowed to stand for half an hour, cold water added and the solution filtered by decantation five times ; finally the silica is transferred to the filter, washed, brought into the crucible while wet and slowly ignited ; any black particles in the silica show insufficient washing. The silica is then evaporated with HF and the alumina and iron remaining subtracted from the amount of silica obtained. The alumina is precipitated as usual ; the precipitate after weighing is dissolved and any residue of silica added to that first obtained. Clay which has been burned before analysis is very hard to decompose and yields an impure silica.

Determination of the Sand.—After treatment with sulphuric acid the clay is filtered and washed, dried and then allowed to stand exposed to the air, so that alteration during weighing is not to be feared. Two portions are then taken. In one the moisture is determined by ignition, and in the other the soluble silica by boiling with alkali.

Volumetric Estimation of Alumina in Caustic Soda.—R. Gatenby, Chem. News, 55, 289. "Take first the amount of caustic soda present with normal HCl and phenolphthalein. When the phenolphthalein is decolorized we have the amount of caustic soda present. Then put into it a few drops of methyl orange solution and again add normal HCl, stirring well (not heating) until a pink color is

obtained which does not vanish by stirring for a few seconds. The number of c. c. of normal HCl required by the second titration equals amount of alumina and alkaline soda salts present. Then add litmus solution, and titrate back with normal caustic soda until a decided blue color appears. Each c. c. of normal caustic soda required = 0.0257 of alumina. The process is very rapid and accurate enough for technical use."

Volatilization of Gallium Chloride.—Lecoq de Boisbaudran finds (Ann. Chem. Phys. [6], 11, 429) that on evaporating a solution of gallium chloride to dryness there is a sensible loss from volatilization, amounting with 0.0789 gms. Ga_2O_3 to 0.00105 gms. in two successive evaporations at 100° to 125° . Where solutions contain gallium chloride it is necessary to evaporate in an apparatus which allows the vapors to be passed through a potash solution to catch the volatilized gallium chloride. If sulphuric acid is present in the solution there is no loss when as much as .0800 gms. Ga_2O_3 , as chloride, is evaporated to dryness and heated to redness.

A New Reaction for Copper.—Aliamet, Bull. soc. chim., 47, 754. When a mixture of sodium sulphite and pyrogalllic acid, in solution, is added to a copper salt, a red coloration, like that of ferric thiocyanate, is produced. The reagent will show the presence of 1 part of copper in 3,000,000 parts of water with ease.

The Estimation of Gold and its Separation from the Platinum Metals.—L. Hoffmann and G. Krüss, Ann.d. Chemie, 238, 66. Gold may be completely precipitated from its solutions with sulphurous acid. The method has the advantage over the oxalic acid method that there is no danger of loss from spirting; and over the ferrous chloride method that the gold obtained is more easily washed. By this method the authors obtained 99.915 per cent. of the amount taken. The solution should not be too dilute or the gold will come down in a very fine powder which is liable to pass through the filter. Even from very dilute solutions, the gold may be precipitated as a coherent mass by Volhard's method, with elutriated mercuric oxide.

Separation of Gold from Platinum.—Precipitation with oxalic acid gave the best results (100.005 per cent. of amount taken). The gold obtained by precipitation with sulphurous acid (100.54 per cent.) and with ferrous chloride (100.24 per cent.) contained platinum.

Gold and Iridium may be separated perfectly by either method of precipitation.

Gold and Palladium are best separated by means of sulphurous acid.

Gold and Rhodium, and Gold and Ruthenium may be separated perfectly by either method of precipitation. Osmium cannot be present in a solution of gold in aqua regia which has been evaporated to dryness as it volatilizes completely as tetroxide.

W. Bettel states, Chem. News, **56**, 133, that in the separation of gold from platinum by sulphurous acid it is necessary that the solution contain neither too much nor too little free acid—the correct amount is found by practice only. It is possible to secure gold 999.9 fine in this way ; but if too acid, all the gold is not thrown down ; if too nearly neutral, a trace of platinum is precipitated. When the platinum predominates it may be thrown down as double chloride and the gold determined in the filtrate, or the gold may be precipitated first and purified by cupellation with silver and the bead obtained parted.

Bettel denies the statement of Hoffmann and Krüss, that when gold is precipitated with ferrous chloride platinum is also thrown down. He states that the separation is a perfect one and that the gold obtained in this way assays from 999.6 to 999.9 if proper care is taken.

The Estimation of Iron in Chars.—R. Davidson, Jour. Soc. Chem. Ind. **6**, 421. The estimation of the iron in chars is, according to the author, best performed with stannous chloride, the method yielding better and more rapid results than either the bichromate or permanganate methods. For the details of the test analyses I must refer the reader to the original paper.

Apparatus for the Determination of Methane in the Air of Mines.—P. von Mertens, Zeit. anal. Chem. 26, 42. The apparatus consists of the measuring tube *M*, which contains 50 c. c., the level tube *N*, the absorption tube *A*, the combustion chamber *T*, and the pressure bottle *W*. The tubes *M*,

N and *A* are enclosed in a glass box which is filled with water. *d* is first brought into position *a-b*, and by pressing on *B*, and opening *C* water is forced into *M* until it is completely filled. *d* is then brought into position *a-d*, the flask containing the gas attached to *γ* and the gas passed through until the capillary is filled; *d* is then brought into position *a-b* and the gas passed into *M* until the water falls slightly below the 0 mark when *5* is closed. By means of the flask *W* the gas is now compressed until the water rises to the 0 mark and then *3* is opened for a moment to bring the gas to atmospheric pres-

sure. To be certain of this the cock 5 is opened and the water in the level tube allowed to run out until it reaches the same level. 5 is now closed and the gas driven over into the U tube *A* where the CO_2 is absorbed. It is then passed into *M* and the absorption measured. Cock 1 is now brought into the position *b-c* and the gas driven over into *T*. The palladium spiral is then heated to redness for 5 minutes by an electric current from 3 Bunsen cells and the gas driven into *A*, the carbon dioxide absorbed, then into *M* and again measured. The capillary tube α is made by slipping a rubber tube of small bore inside a large one. When many samples are to be examined a second combustion chamber may be attached to the tube β . When the mine air contains more than 10 per cent. methane it must be diluted with air before burning.

Estimation of Minute Amounts of Iron in Alum.—R. R. Tatlock, Jour. Soc. Chem. Ind. 6, 267, has examined the colorimetric method with potassium thiocyanate and finds that the following process gives the best results: The standard iron solution is made by dissolving 8.606 gms. iron potash alum in a liter of water. Such a solution contains 1 gm. iron in 1000 c. c. This solution is then further diluted for use by adding 1 c. c. to 99 c. c. water. This dilute standard solution will not keep and must be made up freshly for each operation; such a solution will contain 0.00001 gm. Fe in 1 c. c.

One gm. of the finely powdered alum to be tested is placed in a test-tube holding 30 c. c. and having three marks of $7\frac{1}{2}$, 10, and 20 c. c. 1 c. c. normal iron-free sulphuric acid added, filled to the $7\frac{1}{2}$ c. c. mark with water, heated gently to dissolve the alum, the solution cooled, 0.2 gms. iron-free ammonium thiocyanate added and made up to 10 c. c. with water.

In a second similar test-tube go through the same operation, using 1 c. c. of the dilute iron solution instead of the alum. Ether is now added to both tubes up to the 20 c. c. mark and the tubes agitated. Let the contents of the tubes settle and compare the tints of the ethereal solutions. If not alike make a second trial using more or less iron solution as the first trial indicates. If greater exactness is desired the

ether solutions can be drawn off, the extraction repeated with fresh addition of ether as long as any color is extracted ; the ether extracts made up to the same volume and the colors compared.

The operations should be conducted in a moderate light, as strong sunlight bleaches the ethereal solution. The color of such a bleached solution will return on standing in moderate light. Presence of strong oxidizing substances, and especially hydrogen dioxide, should be avoided.

IRON AND STEEL.

EDITED BY P. W. SHIMER.

Rapid Methods for the Determination of Silicon, Sulphur and Manganese.—J. Jas. Morgan, Chem. News, 56, 82. An approximate determination of silicon in iron and steel is made by heating in a muffle, to bright redness, from 1 to 4 grms. of the finely divided sample, until all silicon is oxidized to silica, and any graphite present is burnt off. On treating the roasted mass with hydrochloric acid, all but the silica is dissolved.

A colorimetric estimation of sulphur is made by dissolving 0.5 gm. of the sample in sulphuric acid, and passing the gases evolved through a dilute solution of lead acetate. The brown coloration produced by the sulphuretted hydrogen is compared with that produced by treating a standard steel in the same manner.

For manganese the method is as follows : “In a test-tube, similar to that used for the estimation of carbon, place 0.2 gm. of the sample to be tested, and in a like tube the same quantity of a standard steel, in which the manganese has been carefully determined by weight. To each add 5 c. c. nitric acid, sp. gr. 1.20, and boil in a beaker of hot water until solution is complete. Cool the tubes, and to each add an equal bulk, about 2 c. c., of water ; replace in the beaker, and, after

boiling for a few minutes, add an excess of lead peroxide, which must be free from manganese, and ten drops of nitric acid, sp. gr. 1.42. After boiling for four minutes the tubes are withdrawn and placed in a beaker of cold water."

"When the peroxide of lead has completely settled, transfer 2 c. c. of the clear supernatant liquid of the standard solution to the graduated tube used in the colormetric estimation of carbon, dilute to 5 c. c. with cold water; mix. In a similar tube place the same quantity of the solution of the sample which is being tested, diluting with water until its color is of the same intensity as that of the standard. Read off the number of c. c. to which dilution is carried, from which, by a simple calculation, the percentage is easily determined."

The Estimation of Silicon in Iron and Steel.—Thomas Turner, Chem. News, 56, 49. The author finds that, in many pig irons, the silicon results obtained by solution of the iron in dilute sulphuric acid, and evaporation to concentration, yield a silica which may be nearly white, and yet contain in some cases 20 per cent. of substances other than silica. The silica thus obtained was found to contain very appreciable amounts of titanium, phosphorus and iron. [In pig irons containing titanium the silicon is best determined by the nitric and sulphuric acid method. Titanium in iron is probably in all cases present as a carbide. This carbide is easily soluble in nitric acid, and, on addition of sulphuric acid, and evaporation to concentration, the titanium remains in solution, and a pure silica is obtained. When the silica obtained by other methods contains titanous acid, it is certain to contain also phosphoric acid and iron, for these form a compound very difficultly soluble in acids. For investigations on the subject of the determination of silicon and titanium in iron, and the complications arising from the presence of titanous acid and phosphoric acid, see Transactions American Institute of Mining Engineers, VII, 346, VIII, 508, X, 137, XV, 455. S.]

Determination of Metallic Iron in Slags.—G. Neumann, Zeit. Anal. Chem. 26, 530. The author determines that part of the iron which is present in the metallic state in slags

by measuring, in a specially constructed apparatus, the volume of hydrogen evolved on treatment with an acid. The results are satisfactory, there being, according to the author, no loss of hydrogen by reduction of oxide of iron.

Volumetric Method for the Determination of Carbon in Iron.—T. Wiborgh, *Berg—und Huettenmaennische Zeitung*, **23**, 223. From 0.1 to 0.2 grm. of the finely divided iron is treated with a copper sulphate solution and the precipitated copper, and possibly still unattacked iron, are dissolved in a mixture of sulphuric acid and chromic acid. The volume of the resulting carbonic acid is measured in a special burette.

Inorganic Standards for the Colorimetric Carbon Test.—Theodore W. Robinson, *Trans. Am. Inst. Min. Eng. Duluth Meeting*, July, 1887. The author uses, for colorimetric carbon tests, permanent standard solutions made by mixing in suitable proportions solutions of the chlorides of cobalt, copper and iron. Solutions thus prepared are constant for four or five months of continued use. Standards for use at night are made on the same principle as day-standards, with the simple modification that the matching with standard steel solutions is done in a dark room, by the aid of kerosene light.

The Influence of Phosphorus Combinations on Iron.—Leop. Schneider, *Oesterreichische Zeitschrift für Berg—und Hüttenwesen*, July 30, 1887. The author does not believe that any large proportion of the phosphorus of bar-iron can exist as phosphate. It would require 15–20 per cent. of puddle-slag containing 1–2 per cent. phosphorus, to introduce 0.3 per cent. phosphorus into the steel. Phosphide of iron is slightly attacked by a neutral, cold solution of cupric-ammonium chloride, the more so the more finely divided the phosphide. One gram of white iron containing 2.06 per cent. phosphorus was allowed to stand 24 hours in a solution of cupric-ammonium chloride, and then filtered. The filtrate contained no trace of phosphorus. The insoluble residue was shaken up for 5 minutes with a 1 per cent. solution of HCl. 0.105 per cent. of phosphorus went into solution as phosphate. On treating the residue again for some hours with

the 1 per cent. solution of HCl only 0.02 per cent. phosphorus went into solution. The residue was again allowed to stand 24 hours in a solution of cupric-ammonium chloride. 0.08 per cent. phosphorus could now be dissolved from the residue by 1 per cent. HCl solution. The residue was once more treated for 48 hours with the copper solution, after which it again gave up 0.09 per cent. phosphorus as phosphate to the dilute HCl solution. It is clear that a water solution of cupric-ammonium chloride attacks phosphide of iron, but, instead of going into solution, it remains in the residue as a basic salt easily soluble in 1 per cent. HCl solution. An alcoholic solution of the copper salt dissolves the phosphate thus formed.

Two Conditions of Phosphorus in Iron.—Byron W. Cheever, Trans. Am. Inst. Min. Eng., July, 1887. The author seeks to prove the presence of phosphates in large proportion in certain irons by volatilizing the iron as chloride with pure chlorine. The phosphorus remaining in the residue is that part present as phosphate. In one case 90 and in the other case 100 per cent. of the phosphorus of weld-metal appears as phosphate.

Colorimetric Determination of Phosphorus in Iron and Steel.—M. F. Osmond, Bulletin Société Chimique, 47, 745. The method is based upon the fact that when phospho-, arseno-, silico-molybdates or their alkaline salts are dissolved in a hydrochloric acid solution of stannous chloride, an intense blue coloration is obtained proportional to the amount of dissolved molybdic-derivative.

ASSAYING.

EDITED BY F. C. BLAKE.

Silver Containing Bismuth.—Wm. Gowland and Yoshimasa Koga, Jour. Chem. Soc., May 1887, 410. The experiments recorded in this paper were made to determine the effect of small quantities of bismuth upon the ductility of silver and

the uniformity of composition of silver bullion bars. The latter has an important bearing on the proper method of sampling silver bars that contain small amounts of bismuth. It is found that concentration of silver occurs throughout the internal portions of the upper two-thirds of the ingot ;—that is, in these parts that remain longest fluid—and notably along the median line of the upper surface. The upper outside edges are lower in silver than the average fineness and lower than the bottom edges. The bottom longest edges throughout their central parts assay as near to the average or poured sample as any outside portion of the bar. The results show that in silver—even of high fineness—suspected to contain bismuth, the portion required for assay should be taken from the metal while melted, and be granulated in water. Should it be impossible to melt the bullion, assay pieces cut from the middle of the bottom long edges will give the fairest representation of the ingot. (These bottom edges are the portions most likely to be almost instantly solidified when the bar is poured, and consequently to be similar to the sample poured into water. This fact is noticed in ingots of other impure metals which change in chemical composition and physical structure during slow solidification. The results indicate that the poured sample taken in these experiments was very slightly enriched. There is more or less liability to enrichment of the poured sample according to the amount of the impurity and its easy oxidization, and it is always necessary to pour quickly from the sample ladle and to avoid filling the ladle from the upper or near surface portion alone of the melted bullion in the crucible.

MINERAL ANALYSIS.

EDITED BY JOHN EYERMAN.

Schorlomite as a variety of Melanite.—By Geo. A. Koenig, Ph. D. On the basis of a *titanium Melanite* from a new locality in Southwestern Colorado, the hypothesis is proposed that *Schorlomite* from Magnet Cove, Ark., may be considered

as a melanite in which titanium replaces both silicon and aluminum. By a series of analyses of schorlomite and melanite, it is proposed to establish the above hypothesis beyond doubt. The following results are merely given as preliminary information.

The material from Colorado, obtained through Moritz Stockder, M. E. at Lake City, shows the melanite as black masses imbedded in a greenish yellow, fine granular matrix, with undefined boundaries. No crystal planes were observed. The color is deep black, brownish at thin edges, and in thin plates. It has an uneven fracture, rather resinous lustre. Sp. gr. = 3.689. Thin sections under microscope show the homogeneous character and optical indifference of the substance.

B. B. Several splinters fused at 3 with slight formation of bubbles (CO_2). Hydrochloric acid decomposes the mineral slowly.

The analysis gave in two determinations :

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2
30.71	8.11	2.26	22.67	34.29	0.304	1.48=99.82

0.5 gr. decomposed in sealed tube required 2.2 c.c. of permanganate (titre=0.0058 Fe). $\text{TiO}_2 + \text{Al}_2\text{O}_3$ were separated from Fe_2O_3 by $(\text{NH}_4)_2\text{S}$ in tartaric solution, and Al_2O_3 from TiO_2 by acetic acid according to Gooch.

Assuming that Ti replaces Si the ratio is obtained $(\text{Si}, \text{Ti}) \text{O}_2 : (\text{FeAl})_2\text{O}_3 : \text{CaO} = 3.728 : 1 : 3.49$. But assuming that Ti replaces the sesquioxides in part as Ti_2O_3 , we obtain 3.28 Ti_2O_3 as replacing alumina=3.64 TiO_2 . It having been ascertained that the loss by ignition is owing to CO_2 and not to water, its equivalent of CaO was subtracted. Thus corrected the composition of the mineral is—

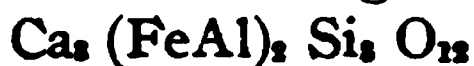
SiO_2	=	30.71	:	60	=	0.5120	}	0.568
TiO_2	=	4.47	:	80	=	0.0560		
Ti_2O_3	=	3.29	:	144	=	0.0230	}	0.187
Fe_2O_3	=	22.67	:	160	=	0.1420		
Al_2O_3	=	2.26	:	103	=	0.0220	}	0.580
CaO	=	32.41	:	56	=	0.5730		
MgO	=	0.30	:	40	=	0.0070	}	
MnO	=	tr.						
CaCO_3	=	3.36						

99.47

This gives the ratio—



quite satisfactory to the formula of garnet



The greenish yellow matrix shows under the microscope an intimate mixture of three minerals, one of which is calcite, one a green and one a white silicate. Its composition is given without at present expressing an opinion as to its mineral nature. Sp. gr. 3.137.

SiO ₂	TiO ₂	Al ₂ O ₃	CaO	FeO	MgO	K ₂ O	Na ₂ O	CO ₂ +H ₂ O
40.76	1.21	8.20	29.60	3.98	5.62	0.89	0.96	6.96
								<hr/> 98.18

A specimen of schorlomite from Arkansas was analyzed with great care to test the hypothesis that schorlomite is simply a titanium melanite. The material was like anthracite in lustre and color, quite opaque, even in thinnest sections. It decomposes readily in HCl. The reduced permanganate was calculated as Ti₂O₃.

Sp. gr. = 3.876 at 23°C.

$$\left. \begin{array}{l} \text{SiO}_2 = 25.80 : 60 = 0.430 \\ \text{TiO}_2 = 12.46 : 80 = 0.156 \end{array} \right\} 0.585$$

$$\left. \begin{array}{l} \text{Ti}_2\text{O}_3 = 4.44 : 144 = 0.031 \\ \text{Al}_2\text{O}_3 = 1.00 : 103 = 0.009 \\ \text{Fe}_2\text{O}_3 = 23.20 : 160 = 0.145 \end{array} \right\} 0.185$$

$$\left. \begin{array}{l} \text{CaO} = 31.40 : 56 = 0.561 \\ \text{MgO} = 1.22 : 40 = 0.030 \\ \text{MnO} = 0.46 : 71 = 0.006 \end{array} \right\} 0.597$$

99.98

giving the ratio—



While not so near to the normal ratio, it is near enough, especially considering the difficulty of estimating Ti₂O₃, in warranting the hypothesis that schorlomite has the formula of garnet, is isomorphous with it, and exists, as the writer hopes to establish, in a complete series of intermediate members ; so

much so, that it will be impossible to say where melanite stops and schorlomite begins, even though every titanium melanite be not called schorlomite.

Meteorite from Australia.—L. Fletcher (Mineralogical Magazine, July, 1887) describes and gives an analysis of a meteorite found in 1884, in Youndegin, Western Australia. The analysis afforded—

Fe	92.67
Ni	6.46
Co	0.55
Cu	trace
Mg	0.42
P	0.24
S	none
Insol. cubes	0.04
	<hr/>
	100.38

Associated with the above meteorite was a very interesting cubic form of graphitic carbon which the author describes and names *Cliftonite*, after Prof. R. B. Clifton, of Oxford.

Muscovite from Alexander Co., North Carolina.—F. W. Clarke (Studies in the Mica Group, Am. Jour. Sci. Vol. 34, Aug. 1887, 131) gives an analysis of muscovite, from near Stony Point, Alexander Co., N. C.

Ignition	5.46
SiO ₂	45.40
TiO ₂	1.10
Al ₂ O ₃	33.66
Fe ₂ O ₃	2.36
MgO	1.86
Li ₂ O	trace
Na ₂ O	1.41
K ₂ O	8.33
F	.69
	<hr/>
	100.27
less O	.29
	<hr/>
	99.98

Howlite from Nova Scotia.—Penfield and Sperry in an article on the Chem. Comp. of Howlite (Amer. Jour. Sci., Sept., 1887, p. 220) give the following analysis after deducting 4.32 per cent. of gypsum corresponding to 2.01 per cent. of SO_2 .

SiO_2	15.33
B_2O_3	44.52
CaO	27.94
Na_2O	.53
K_2O	.13
H_2O	11.55
	<hr/>
	100.00

Formula of this acid silico-borate is $\text{H}_5\text{Ca}_2\text{B}_6\text{SiO}_{14}$.

Destinezite from Vise.—G. Cesáro (Jahrb. f. Min. 1887, 1, 412) gives analysis of a whole destinezite—

					Hygroscopic	
res	Fe_2O_3	P_2O_5	SO_3	H_2O	H_2O	
1.40	37.60	16.79	18.85	25.35	0.30	100.26

Formula—



ORGANIC ANALYSIS.

The Estimation of Organic Bodies by Oxidation with Potassium Permanganate.—J. H. Smith, Jour. Soc. Chem. Ind. 6, 98, 260. The author has examined the action of potassium permanganate and manganese dioxide upon organic substances in acid, neutral, and alkaline solutions. I shall confine myself to a very brief statement of the results obtained in acid (sulphuric) solution. The reader should consult the original paper which is well worth careful study.

Smith finds that the oxide which is precipitated when organic substances are treated with KMnO_4 always contains the manganese as MnO_2 . When organic substances are boiled with KMnO_4 in excess in acid solution, and the amount of KMnO_4 in excess estimated by ferrous sulphate, the KMnO_4 destroyed is in excess of the calculated amount necessary to

effect complete oxidation to CO_2 and H_2O . This he finds to be due to the action of the KMnO_4 upon the manganese precipitate, whereby oxygen is set free and the KMnO_4 reduced to MnO_2 . This action of KMnO_4 upon MnO_2 may be almost destroyed by adding ferric phosphate to the solution. By this modification of the ordinary oxidation process with permanganate it is possible to convert it into a rapid analytical method, sufficiently accurate for many purposes.

Acetic acid is scarcely at all oxidized in acid solution. Hence, where acetic acid is one of the products of oxidation the full theoretical amount of KMnO_4 is not used. An instance of this is found in common alcohol which required 32.2 per cent. of the theoretical amount needed to convert it into CO_2 and H_2O ; and perhaps also in the case of cane sugar where 82.2 per cent. was required. The importance of Smith's work is very great and its bearing upon the determination of organic matter in water analysis, and in many other determinations is obvious. He promises a further, detailed account of the application of this method at a future time.

The Estimation of Nitrogen.—M. Raulin, Bull. soc. chim., 47, 94. The author describes an apparatus by the use of which the Dumas method for the estimation of nitrogen is made more speedy and practical. A Deville apparatus supplies the carbonic acid used in the operation. The combustion tube, which is about 1.8 m. long and 18 m. m. internal diameter, is of copper and is surrounded by four cylindrical brass water-jackets, two at the extremities and the others between and equidistant from each other. These are 10 c. m. in length and 5 m. m. from the surface of the combustion tube. They are connected with the water supply and with each other by means of caoutchouc tubes. A charge of copper foil, copper oxide and the organic matter to be analyzed is placed in each of the intervals in the tube between the water-jackets, the tube thus containing the materials for three analyses. After the expulsion of the air in the tube by the carbonic acid, a current of water is passed through the cooling apparatus and the charge in the interval nearest the receiver heated by means

of a small combustion furnace 25 c. m. long. The nitrogen is collected in a graduated cylinder inverted over caustic potash solution, another cylinder of the same size being inverted over the same solution for the purpose of making necessary corrections. When all of the nitrogen has been expelled from the first charge, the gas in the cylinder is washed with the potash solution by means of a pipette of a peculiar form, described by the author, and the reading made. The gas is then removed by the pipette and the furnace placed under the next charge which is decomposed in the same manner. When all three charges have been heated and the nitrogen removed from the cylinder, the carbonic acid is passed through the tube for a time equal to that required for one of the determinations, and the amount of oxygen and nitrogen derived from the carbonic acid apparatus thus determined, for which allowance is made in the calculations, in which also the amount of gas in the second cylinder is taken into consideration. For details of the operation and apparatus the original paper must be consulted.

I. A. P.

Separation and Estimation of Carbon Oxysulphide.—P. Klason, Jour. prak. Chem. **36**, 71, finds that carbon oxysulphide is completely absorbed by a solution made by dissolving one part caustic potash in two of water and adding an equal volume of alcohol. The mixture of gases in which carbon oxysulphide is to be determined is first passed slowly through potash lye, which absorbs all acid gases, then through triethylphosphine, or a strongly acid solution of copper sulphate to remove sulphuretted hydrogen, and then through the above solution to remove carbon oxysulphide.

The Estimation of Thiocyanic Acid.—P. Klason, Jour. prak. Chem. **36**, 74. Thiocyanic acid may be estimated with as great exactness as hydrochloric; either by the method of Mohr in neutral solution, using potassium chromate as indicator; or by Volhard's method, using ferric alum as indicator. It may also be estimated by permanganate but the results obtained by this method are too low. The deficiency increases on diluting the solution.

On the Estimation of Methyl Alcohol in Presence of Ethyl Alcohol.—Herner, *The Analyst*, 12, 25. Dupre's method of oxidizing a known quantity of the alcohol with $K_2Cr_2O_7$ acidified with H_2SO_4 and distilling from an oil bath the acetic acid formed, and estimating by deci-normal soda, is improved by measuring the quantity of chromate reduced instead of the acetic acid obtained. Same solutions required as in "Estimation of Glycerine in Fats." (See p. 448.) A. L. COLBY.

Detection and Estimation of Starch in Liquids Containing Dextrine.—G. Burkhard, *Chem. Zeit.* 11, 1158. If alcohol is added to the solution until a faint turbidity appears, the liquid warmed until this disappears and tannic acid solution added, all the starch will separate on cooling as a flocculent precipitate. This precipitate when washed with alcohol loses all its tannic acid and pure starch is left behind. If only the qualitative test is required, the filter is dried, spread on a glass plate and moistened with a few drops of dilute iodine solution, which produces an intense blue color. It is easy to distinguish between this color and the blue communicated to most filter paper by iodine solution.

If the starch is to be determined quantitatively it is washed thoroughly with alcohol, placed, together with the filter, 20 c. c. water and 1 c. c. normal sulphuric acid, in a pressure flask, and heated in the paraffine bath for 4 hours to convert the starch into sugar; the sugar is then determined with Fehling's solution. The amount of sugar multiplied by 0.9 gives the starch.

On the Admixture of Starch with Yeast.—Stock, *The Analyst*, 12, 84. Starch is added to yeast infested with ferments other than the true *torula*. It improves its looks and impedes development of foreign germs. Starch of potato, maize, rice, arrowroot, and buckwheat are used.

For potato and arrowroot starch use method of deposition. 25 grms. of sample rubbed with 50 c. c. cold water, transferred to 30 oz. beaker. 5 grms. pure potato farina similarly treated. Contents of beakers washed by decantation until rate of deposition is alike in each. Then decant perfectly clean water

from beaker containing sample, wash starch onto filter, wash twice with alcohol, once with ether, dry gradually, finally at 100° C.; weigh. In analyzing yeast mixed with arrowroot, use arrowroot starch for standard of deposition.

In analyzing yeast adulterated with the other starches, prepare a milk of 5 grms. of sample, and 5 of pure yeast adulterated with 20 per cent. of same variety of starch. Count the iodized granules over 10 fields of the two samples by aid of a microscope with cross hairs in eye piece. From data calculate per cent. of adulteration.

A. L. COLBY.

The Estimation of Starch.—Dr. J. Effront, Bull. soc. chim., 47, 5. The author's method is based upon the fact, which he ascertained, that in a liquid containing dextrine and sugars the latter can be destroyed by means of ammonia, sodium hypochlorite and hydrochloric acid without affecting the former. The amount of dextrine is determined by the difference of rotatory power which the liquid possesses before and after the destruction of the sugars. Soleil's saccharimeter is used. The liquid is first concentrated until it contains 4 to 9 per cent. of sugar and its rotatory power determined. 10 c. c. of this solution is mixed with 10 c. c. of ammonia, of .92 sp. gr., and 5 c. c. of water. The whole is then placed in a 300 c. c. flask, tightly corked, with the cork secured by a string, and the flask immersed in a vessel of cold water. The temperature of the water in the vessel is then raised to boiling and kept so for 40 minutes. The flask is then allowed to cool, the contents poured into another flask with a long neck and the liquid concentrated to 5 to 8 c. c. It is then cooled again and poured into a vessel immersed in cold water. 10 c. c. of sodium hypochlorite solution, containing 7 to 8 per cent. of active chlorine, is now added, the mixture stirred and 2 c. c. of concentrated hydrochloric acid added. The liquid is next poured into a graduated cylinder and the volume diluted to 25 c. c. The rotatory power of the liquid is now taken, remembering that the original solution was but 10 c. c., and the calculations made according to prepared tables.

The author says that according to some authorities there are as many as nine dextrines, but he has found by a number of comparative experiments that if they exist they all possess the same rotatory power. The only source of error is the liability of part of the dextrine being converted into glucose if the operation of heating be long continued.

For the approximate determination of starch in flour or in raw grain the author uses a modification of Dubrunfaut's method and operates as follows :

Five grams of the substance and 20 c. c. of concentrated hydrochloric acid are placed in a mortar and stirred until complete solution, which, in the case of starch or flour, takes place in from 6 to 8 minutes. With raw grain solution is difficult and requires 30 minutes, a small amount of glucose being formed, which increases with the length of treatment. Water is then added, sufficient to increase the volume to 200 c. c., and the solution filtered. The dextrine formed is then determined by the saccharimeter. Treatment with strong acid longer than absolutely necessary for solution vitiates the results. With crude grain results are within 2 to 3 per cent. of the total starch. With starch and flour the method is much more exact.

For very accurate determinations of starch in grain the author uses Mercker's method as far as the conversion of the starch into dextrine and maltose, and then takes the rotatory power of the liquid, destroys the sugar with ammonia and sodium hypochlorite and proceeds as described above. Results are thus obtained within .2 to .4 per cent. of the total starch. The author gives a number of tables comparing results obtained by his method with those obtained by other methods.

I. A. P.

Comparative Sweetness of Cane and Starch (Glucose) Sugars.—Experiments made by T. Schmidt in the laboratory of the German Sugar Association, show that the sweetness of cane sugar is to that of starch sugar as 1.53 to 1.*

These numbers show that glucose is sweeter than is popularly supposed, viz: 2.5 of glucose to 1 of sucrose.

H. W. W.

* Die Deutsche Zucker Industrie, Vol. 12, No. 20, p. 579.

Determination of Ash in Organic Substances.—A. Köb-
rich, Chem. Zeit. II, 1159. When ammonium nitrate is added
to burn off the carbon, the ash is apt to contain nitrates, which
can easily be detected by the ferrous sulphate reaction. In
burning in this way there is also danger of loss by the spirting
of the particles during the heating. To avoid these sources
of error the author directs a stream of oxygen upon the burn-
ing carbon, through a porcelain tube. If the ash melts, en-
closing particles of carbon, it is treated with water and evapo-
rated to dryness; the carbon then floats on the solution during
the evaporation, deposits on the side of the crucible, and is
easily burned off.

Estimation of the Free Acid in Tan Liquor.—R. Koch,
Ding. poly. Jour. 264; 395, 265, 33. A measured amount
of standard albumen solution is added and then standard Ba
(OH)₂ until nearly neutral. Then the solution is heated until
the albumen coagulates and precipitates the tannin. The
cooled solution is now filtered and an aliquot portion of the
clear filtrate titrated with standard barium hydroxide until the
color changes. A correction must be made for acid contained
in the albumen solution added.

**Estimation of Acetic Acid in Acetates by Direct Ti-
tration.**—A. Sonnenschein, Chem. Zeit. II, 591. *Estimation
of Acetic Acid in Sodium Acetate.*—5 gms. of the sample is
dissolved in water and made up to 250 c. c. To 50 c. c. of the
clear solution 3 drops of phenacetolin solution is added and
the solution titrated with HCl until the color changes to yellow.
Each c. c. normal HCl = 5.3 per cent. Na₂CO₃.

Two drops methylorange is now added and then HCl run in
until the color becomes red. Each c. c. normal HCl = 6 per
cent. acetic acid or 8.2 per cent. sodium acetate. An alterna-
tive method consists in treating the solution with BaCl₂ and
filtering. The precipitated BaCO₃ when dissolved and titrated
gives the Na₂CO₃ and the filtrate is titrated for acetic acid as
above. The titration is best carried on in a porcelain dish.
Any carbon present is separated and weighed on a tared filter.
The following results were obtained :

	Distillation Method of Fresenius. Per cent.	Titrated directly per cent.	Per Cent. CH_3COONa		CO_2 calculated as Na_2CO_3		Carb'n	Total
			Fresenius	Direct	Directly with phenacetolin	After precip- itation with BaCl_2		
I.	66.60	66.80	91.02	91.29	6.36	6.15	2.01	{ 99.39 99.65
II.	69.88	69.90	95.50	95.53	—	—	—	

Estimation of Acetic Acid in Acetate of Lime.—5 gms. is dissolved in water and 3 gms. animal charcoal added. This removes the coloring matter. CO_2 is led into the solution to saturate the caustic lime and the solution is then boiled and filtered, made up to 250 c. c. and 50 c. c. titrated with methyl orange and HCl .

<i>Distillation Process.</i>		<i>Titrated Directly.</i>	
Per Cent.	Per cent.	Per cent.	Per cent.
CH_3COOH	$(\text{CH}_3\text{COO})_2\text{Ca}$	CH_3COOH	$(\text{CH}_3\text{COO})_2\text{Ca}$
54.31	71.50	54.44	71.68

Presence of chlorides in the acetates has, of course, no influence on the result of the titration.

Glue Analysis.—R. Kissling, Chem. Zeit. II, 691, 719.

Water Estimation.—2–3 gms. of rasped glue are dried in an air bath at $110\text{--}115^\circ$ until the weight remains constant. At this temperature no decomposition takes place.

Determination of the Ash.—The rasped glue used in the water estimation may be ignited rapidly. Small errors are of no consequence, as only large differences in the amount of ash are of significance. The burning is completed by moistening [with HNO_3 ?] and heating again. The ash from skin glue contains a considerable amount of caustic lime; it is therefore infusible, reacts alkaline, and is generally free from phosphoric acid and chlorine. Bone glue leaves an ash containing alkalis, melts readily and dissolves in water; in the solution in nitric acid phosphoric acid and chlorine may be detected.

Estimation of the Acid.—Thirty gms. glue are treated with

80 c. c. water in a round bottomed flask and allowed to stand for several hours. Steam is then blown through the flask, which is placed in boiling water, and when 200 c. c. of distillate has been collected it is titrated with alkali. Sometimes the distillate contains sulphurous acid, and it is best, therefore, to put a measured amount of titrated alkali in the receiver.

Examination for Drying Power.—The solution of glue which has been freed from acid is made up to 150 gms. and heated in boiling water for some time. 10 c. c. is then poured into a watch glass so as to form a single shallow pool in the center. For comparison, two other samples, one a good and the other a poor glue, are treated in the same way. The three watch glasses are placed in a room as free from dust and draughts as possible, and by observing the way in which they dry a good idea of the value of the sample may be formed.

Insoluble Matter.—Ten c. c. of the above solution is diluted to 1000 c. c. in a graduated cylinder and allowed to stand for 24 hours when the volume of the deposited, insoluble material is read off.

The Odor of the Glue is also of some value as indicating its quality. This should be noted both in the cold glue and in the hot solution.

The paper contains a table giving the results of the analysis of 16 samples. The amount of water found varies from 12.28—18.1 per cent., the ash from 1.26 to 5.07 per cent. and the volatile acid from none to 0.83 per cent.

Quantitative Separation of Ortho and Paratoluidine.—Miniati, Booth and Cohen, Jour. Soc. Chem. Ind. 6, 418. The method of Schoop (Chem. Zeit. 9, 1785) does not give accurate results. When Rosenstiehl's method is used the standard solution should contain 1.059 gms. of the anhydrous acid in 250 c. c. anhydrous ether so that each c. c. equals 0.005 gms. toluidine. The amount given by Rosenstiehl (1.062 gms. per 250 c. c.) is not quite correct. Rosenstiehl's method is impracticable as the precipitate being light does not settle rapidly. It is equally impossible to determine the

end of the reaction by means of litmus paper as recommended by Lorenz, as the change of color is gradual. It was found that the best method was to add excess of oxalic acid solution, filter, wash with ether and weigh on a watch glass. Any residue in the flask and any residue in the filter paper are dissolved in water and titrated with decinomal potash solution. Paratoluidine is only completely precipitated after twelve hours standing. If, however, the mixture is allowed to stand so long 4-5 per cent. of the orthotoluidine comes down. The best way, therefore, is to make first an approximate analysis to determine the amount of paratoluidine present, and then, in a second analysis, to run in just enough oxalic acid to precipitate this and allow to stand twelve hours.

Upon this subject see also C. Häussermann, Ding. poly. Jour. **265**, 42 ; Chem. Ind. **10**, 55.

The Optical Behavior of Cocaine has been studied by O. Antrick, Ber. d. deut. chem. Ges. **20**, 310, who has devised a process for its estimation on this basis, for the details of which I must refer to the original paper.

New Test for Cocaine.—H. MacLagan, Am. Druggist, **16**, 22. "The permanganate test of Dr. Giesel will hardly ever be accepted as a practical one, that is to say one for every-day use, the facility with which that salt is reduced by such an infinite variety of substances being a serious objection to it.

There is not much doubt, however, that the amorphous alkaloid is instantly destroyed by potassium permanganate, while the crystallizable cocaine forms a salt which remains intact for a considerable period ; in fact, the amorphous portion can be almost if not quite entirely removed by this means and the pure crystals obtained.

It is scarcely possible to produce for general use a cocaine salt which is *absolutely* free from the amorphous, and the least trace of this, even a fraction of one per cent., would cause reduction of the permanganate and possible condemnation, especially in the hands of those not fully posted. The writer has been using a test for the past six months, discovered accidentally, which has never yet failed to give satisfac-

tory results. If about one grain of hydrochlorate of cocaine be dissolved in about two fluid ounces of water, one or two drops of ammonium hydroxide added, and the sides or bottom of the containing vessel rubbed with a glass rod, well marked striæ will appear where the rod has touched, and shortly after, flocks of precipitate will form and slowly subside, leaving the liquid clear and bright as at first. If the amorphous salt is present, even in moderately small proportions, no striæ nor precipitate will form, and the liquor will remain milky for a long time, the surface having a more or less oily appearance.

If the amorphous alkaloid is present in considerable quantity, which is nearly always the case when the salt is made from the mixed alkaloids just as obtained from the leaves, it may be partially separated by dissolving about thirty grains in two ounces of water, and adding slowly, drop by drop, a five per cent. solution of ammonia, stirring constantly, until a flocculent precipitate begins to appear. The alkaloid will be found in sticky masses on the glass and rod. It may be obtained in a very pure state by repeated fractional precipitation, stopping each one at the point where the liquor begins to lose its milkiness and loose white flocks appear. The alkaloid obtained in this way, after being deprived of coloring matter if necessary, is a clear, transparent substance of a slightly yellowish color, resembling Canada balsam, but of firmer consistence, and may be lightly touched with the fingers without sticking, at ordinary temperatures. A specimen over six months old fails to show the least sign of crystallization. The hydrochlorate of this alkaloid has the appearance of a varnish-like mass, and cannot be reduced to powder. According to the experience of the writer, the average proportion of this alkaloid in cocoa leaves is about fifteen per cent. of the total alkaloidal yield."

On Valenta's Test for Oils.—G. C. Hurst, Jour. Soc. Chem. Ind. 6, 22. The author has obtained lower turbidity temperatures than either those of Valenta (Ding. Poly. Jour. 252, 296) or of Allen. (Jour. Soc. Chem. Ind. Feb. 1885). Valenta and Allen state that rape oil is insoluble in acetic acid

but the author finds it to be soluble. The turbidity temperature of an oil decreases as the amount of free acid increases. So long as the proportion of oil and acetic acid remain the same it does not matter how much of each is taken. Increase of the proportion of oil lowered the turbidity temperature, while decrease raised it. Mineral oils are only partially soluble in acetic acid. If a fat oil contains only about 10 per cent. mineral oil the oil is completely dissolved by acetic acid. The test is on the whole inferior to Maumene's.

A New Qualitative Test for the Alkaloids Accompanying Sulphate of Quinine in the Commercial Product.—O. Schlickum, Pharm. Ztg., 1887, p. 23. This method is based upon the great insolubility in water of chromate of quinine, one part of it requiring 2000 parts of water for complete solution. If a caustic alkali be added to a cold saturated solution of the chromate no precipitate is produced, as the hydrate possesses nearly the same degree of solubility as the chromate. Hence, if a solution of sulphate of quinine be precipitated by potassium chromate and the liquid allowed to stand until the complete crystallization of the chromate of quinine, no turbidity will be produced in the mother liquor by the addition of caustic soda, if the quinine is pure. If, however, it contains cinchonidine, quinidine, or cinchonine, a white turbidity, or flocculent precipitate, is produced by the alkali. Chromate of cinchonine requires 2000 parts of water for solution, while the hydrate requires 4000 parts. Hence, caustic soda will produce a precipitate in a saturated solution of the chromate. The chromates of quinidine and cinchonidine dissolve in about 400 parts of water, while the bases themselves are much less soluble. Hence, the same results will follow the addition of caustic soda to the mother liquor of these chromates, as in the case of cinchonidine. The author gives the following method for operating the test :

.5 gm. sulphate of quinine and 10 c. c. of water are placed in a test tube, the liquid heated to boiling and .15 gms. pulverized potassium chromate added. The mixture is stirred carefully and set aside for about four hours, the tube being shaken at

intervals. The liquid is then filtered and caustic soda added to the filtrate. If the quinine is pure no turbidity is produced. If, however, there is present in the sulphate of quinine .5 per cent. of sulphate of cinchonine, or 1 per cent. of sulphate of quinidine or cinchonidine, the liquid becomes cloudy and deposits a flaky precipitate on standing some time. It is thus seen that the test is sufficiently delicate to answer all the purposes of the pharmacist. *I. A. P.*

The Analysis of Quinine by the Chromate Process.—O. Hesse, Pharm. Jour., 1887, p. 665. The author has found that DeVrij is not entirely correct when he asserts that the alkaloids accompanying sulphate of quinine remain in the mother liquor when the quinine is precipitated as chromate. Experiments made by him show that the chromates of hydroquinine and cinchonidine possess the property of crystallizing in combination with the chromate of quinine. The mother liquor from the chromate obtained by precipitating a solution of sulphate of quinine containing .3 per cent. of cinchonidine, on being rendered alkaline and evaporated, gives a slight precipitate containing quinine and cinchonidine. The amount of cinchonidine in this precipitate does not, however, increase in proportion to the amount in the original specimen, owing to the fact that part of it crystallizes with the chromate of quinine. Analysis shows this precipitate to be a compound of quinine and cinchonidine in the proportion of one molecule of the former to seven of the latter, expressed by the formula $C_{20}H_{24}N_2O_2 \cdot 7C_{19}H_{22}N_2O$. This accounts for the high results sometimes obtained in the estimation of cinchonidine. Generally, however, these results are too low. If the commercial sulphate of quinine contains much over .3 per cent. of cinchonidine a considerable amount of the latter will be found in the chromate precipitate. The author finds that this precipitate on being treated with ammonia and ether not only furnishes the compound $C_{20}H_{24}N_2O_2 \cdot 2C_{19}H_{22}N_2O$, but also more water of crystallization than is found in combination with pure chromate of quinine. These facts seem to show that cinchonidine in commercial sulphate of quinine cannot be accurately determined by the chromate method. *I. A. P.*

The Estimation of Indigo in Textile Fibers.—Adolphe Renard, Bull. soc. chim., **47**, 41. Ten grams of the dyed fiber is placed in a flask with 200 c. c. of a solution of sodium bisulphite and milk of lime, prepared by adding two liters of water and 100 c. c. of milk of lime to 100 c. c. of neutral sodium bisulphite solution, of 35° B. The flask is heated in an air-bath to 60–70°. The blue color of the fiber vanishes rapidly and the fiber and solution acquire a yellowish tinge. A current of illuminating gas is now passed into the flask and the liquid stirred until all trace of blue has disappeared. The solution is then decanted quickly into a graduated cylinder, while continuing the passage of the gas, allowed to cool and the volume measured, which should be about 100 c. c. After allowing to stand twelve hours the indigotine is precipitated with hydrochloric acid. The precipitate is filtered, washed and dried, dissolved in 10 c. c. of fuming sulphuric acid and the indigotine determined according to Muller's method.

I. A. P.

The Determination of the Coloring Matter, Etc., in Silk.—Jules Persoz, Mon. scien. du Quesn., **545**, 597. A weighed quantity of the silk is first decolorized and cleansed by means of solutions of neutral potassium oxalate, sodium carbonate, caustic soda, or alkaline sulphides, etc., and water. It is then dipped into some dilute hydrochloric acid (sp. gr. 1.06) allowed to remain a few minutes, taken out and dried. This renders the silk brittle. It is next triturated in a mortar with soda-lime and the nitrogen determined by Will and Varrentrapp's method. From the amount of nitrogen the weight of the silky matter in the specimen is calculated. The author has found that pure silk contains 18 per cent. of nitrogen and bases his calculations upon this value. The amount of the silky matter being thus known the percentage of coloring matter, etc., in the finished silk is found by the following formula :

$$C = 100 \frac{P - P_1 \frac{100}{100-n}}{P_1 \frac{100}{100-n}}$$

in which C is the percentage sought, P the weight of the original specimen, P^1 the calculated amount of pure silk, and n the percentage, previously determined, of the gritty matter in the raw silk. The result obtained will thus be a percentage of the weight of the raw silk upon which it is the custom to base all calculations.

For the detection of tin in dyed silks a small amount of the fiber is dissolved in a test-tube in hot, concentrated hydrochloric acid, the solution diluted, filtered if necessary, and a current of hydrogen sulphide passed through the liquid. Any tin present will be precipitated as sulphide.

As a means of distinguishing mulberry silk from "wild" silk—that from the *bombyx pernyi*, *mylitta*, etc.—the author has found that specimens of the latter variety dissolve in a boiling solution of zinc chloride only if the reagent is concentrated and marks 60° Baumé, while mulberry silk dissolves readily if the solution be diluted to 45° Baumé. By this means a quantitative separation of the two varieties can be effected.

I. A. P.

Examination of Artificial Coloring Matters.—E. Weingärtner, Ding. poly. Jour. **264**, 85.

I. SOLUBLE COLORS.

Part of the aqueous solution is treated with tannin solution (25 parts tannin, 25 parts sodium acetate and 250 parts water.)

(A) A precipitate forms.

Basic Colors.

The aqueous solution is reduced with zinc dust and HCl, neutralized, and a piece of filter paper dipped in the solution and exposed to the air.

<i>The color reappears on the filter paper.</i>					<i>The filter paper remains white.</i>
<i>Red</i>	<i>Yellow and Orange</i>	<i>Green</i>	<i>Blue</i>	<i>Violet</i>	<i>Yellow-Brown-Blue</i>
Fuchsine	Phosphine	Malachite Green.	Methylene Blue.	Methyl Violet.	Chrysoidine
Toluylene	Flavanaline	Brilliant Green.	New Blue.	Hoffmans Violet.	Vesuvine (Bismarck brown)
Safranine		Methyl Green.	Muscarine	Mauveine	Auramine.
				Amethyst	Victoria blue
				Crystal Violet.	Methylene green

(B) No precipitate forms.

Acid Colors.

The aqueous solution is reduced with zinc dust and HCl (or ammonia.)

The solution is decolorized.					The color changes and becomes brownish-red. Upon paper the the color becomes like that of the ammoniacal solution. Alizarine S Alizarine Blue S Coeruleine S
The original color reappears upon paper.		The original color does not reappear.			
The aqueous solution is acidified with HCl and then treated with ether.		The color is heated upon platinum foil.			
The ether dissolves the color and the aqueous solution becomes almost colorless.	The ether remains colorless	Deflagrates without evolution of colored vapors.	The color burns slowly or deflagrates slightly and colored vapors form.		
			The watery solution is heated with unmordanted cotton.		
Phtaleine	Sulphona- ted rosani- line deri- vatives Sulphona- ted Indu- lines	Nitro colors (nitrophenol)	The color upon the cotton re- sists a warm soap solution.	The color is re- moved by a warm soap so- lution.	
			Benzidine Azocolors	Azocolors Erythroseine	

II. COLORS INSOLUBLE IN WATER, SOLID OR IN THE FORM OF PASTE.

The color is treated with water and several drops of a 5 per cent. caustic soda solution.

The color dissolves.		The color does not dissolve.			
The alkaline solution is filtered, sink powder added and brought upon filter paper.		The color is heated with 70 per cent. alcohol.			
The color of the alkaline solution reappears.		It dissolves.		Does not dissolve	
	The color does not reappear; or the color changes during the reduction and the new color is permanent.	The alcoholic solution fluoresces.		The solution does not fluoresce	
		33 per cent. caustic soda is added.			
		The color changes to a reddish brown.	No change of color.	The fluorescence disappears.	The fluorescence does not disappear
Coeruleine	Canarine	Induline	Indophe-	Magdala	Primrose
Galleine	Alizarine	Nigrosine	nole	red	Cyanosine
Gallocyanine	Anthrapurpu-	Rosaniline			
Galloflavine	rine	Blue			
	Flavopurpu-	Diphenyl-			
	rine	amine			
	Nitro alizarine	blue			
	Alizarine bro'n				
	Alizarine blue				
	Chrysamine				
	Solid green				
	Dinitrosoresor-				
	cine				

The above tables can only be used where a single color is at hand ; not for mixtures. In using it, after reduction with Zn and HCl the solution is treated with sodium acetate so that free HCl will not be present. In group *B* the reduction must be made in acid solution (Zn and HCl) when yellow, orange, Ponceau and Bordeaux colors are present. Alizarine S is very difficult to reduce completely, and if the reduction is carried too far the color will not reappear.

Estimation of Phenylhydrazine.—E. V. Meyer, Jour. prak. Chem. **36**, 115. The very dilute solution of the base or its hydrochloride is added to an excess of .5% iodine solution and the excess of iodine determined with sodium thiosulphate. The reaction is as follows : $C_6H_5NH-NH_2 + I_2 = 3HI + N_2 + C_6H_5I$.

Detection of Saccharine.—Orthosulphamine benzoic acid, the so-called "Fahlberg's Saccharine," has lately been put upon the market by Fahlberg, List & Co., and is for sale in this country by their agents. It is recommended by them "as an excellent corrector of the bitter taste of alkaloidal salts, for the manufacture of black licorice and chewing tobaccos, also for champagne, lemonades, liquors, conserves, fruit-juices, chocolate and candies." Methods for detecting and estimating it will therefore be needed at once.

Schmitt, Rep. anal. Chem. **7**, 437, has devised the following method for its detection in wine : 100 c. c. of the strongly acidified wine is shaken three times with 50 c. c. of a mixture of equal parts ether and petroleum spirit, the decanted ethereal solution evaporated to dryness after addition of a little caustic soda (caustic potash will not answer). The residue is heated, in a silver or porcelain dish, one-half hour at 250° C. It is now dissolved in water, acidified with sulphuric acid and extracted with ether which dissolves the salicylic acid formed from the decomposition of the ortho sulphamine benzoic acid. The ethereal solution is then evaporated to dryness and the salicylic acid tested for with ferric chloride. In this way less than 0.005 per cent. can be readily detected.

Test for Saccharine in Sugar.—Reischauer, Ding. poly.

Jour. 264, 571. The sugar is extracted with ether. If the sugar is alkaline, a strong solution acidified with phosphoric acid is used. The ether is distilled off and the residue fused with a mixture of soda and saltpeter (6:1). This converts the sulphur into sulphuric acid which can be detected with barium chloride.

Estimation of Carbonic Acid in Beer.—C. A. Crampton and T. C. Trescott, Amer. Chem. Jour. 9, 290. The cork of the bottle containing the beer is perforated with a champagne tap and this is connected with an Erlenmeyer flask in the broad bottom of which the bubbles are broken; this is connected with a sulphuric acid tube then a calcium chloride tube and, finally, a soda-lime tube to absorb the carbonic acid. The bottle of beer is heated in a can containing water and air free from CO₂ drawn through the apparatus. The ordinary champagne taps have a thin edged thread which cuts the corks too much and this is turned off smooth before use. When the beer is contained in patent rubber stoppered bottles the CO₂ is estimated by the loss of weight; the bottle, sulphuric acid and calcium chloride tubes being weighed together on a large balance, the stopper removed and connection made with the tubes as rapidly as possible.

Quantitative Estimation of Glycerine in Wine and Beer.*
—The principle of the estimation is based on the reaction of glycerine with benzoylchloride forming esters containing one, two and three molecules of the benzoic acid radicle respectively. These compounds are represented by the following symbols :

Monobenzoate, $C_3H_5 \begin{matrix} (OH)_3 \\ C_7H_5O_2 \end{matrix}$

Dibenzoate, $C_3H_5 \begin{matrix} (OH) \\ (C_7H_5O_2)_2 \end{matrix}$

Tribenzoate, $C_3H_5 = (C_7H_5O_2)_3$

When 0.1 gram glycerine is treated in a flask with 10–20 c. c., water, 5 c. c. benzoylchloride and 35 c. c. 10 per cent. soda lye, for 10 to 15 minutes, with constant cooling and shak-

*R. Diez, Zeit. f. Physiologische Chemie, Vol. XI, p. 472.

ing there is formed .385 grams of the ethers already mentioned.

Before heating the ether with the benzoylchloride, all carbohydrates must be carefully removed for they also give insoluble ethers.

Wines Poor in Sugar.—Take 20 c. c., and after driving off the alcohol, evaporate almost to dryness with an excess of lime (for every 2 grams of extract use 3 to 4 c. c. of 40 per cent. cream of lime). The residue is now exhausted, (hot,) with 20 c. c. 96 per cent. alcohol. After cooling, add 30 c. c. ether and filter, wash the filter with a mixture of two parts absolute alcohol and three parts ether

Evaporate the filtrate and dissolve the glycerine in 10 to 20 c. c. water, and treat with 5 c. c. benzoylchloride and 35 c. c. 10 per cent. soda lye, with constant shaking and cooling for 10 to 15 minutes.

The ether is then collected in a filter, washed and dried at 100°C., for 2 to 3 hours. Each .385 grams corresponds to 1 gram of glycerine.

Wine Rich in Sugar.—Add one gram of sand to the lime used in drying. Double the quantity of alcohol and ether mentioned above.

Beer.—Evaporate 50 c. c. nearly to dryness with lime and sand. Rub the cooled residue to a fine powder and treat with 50 c. c., 96 per cent. alcohol. This extraction should be made in a continuous extraction apparatus. To the extract add 75 c. c. ether, filter and evaporate filtrate. Dissolve the glycerine obtained in 5 to 10 c. c. water, add 2 to 3 c. c. benzoylchloride with 14 to 20 c. c. soda lye and treat as before described.

The estimation of glycerine as benzoate in accordance with the method described, has the following advantages over other methods in use.

1. Quicker and easier manipulation, further the less danger from loss, since the operation is carried on with smaller quantities of liquid and a non-volatile substance is weighed.

2. The weighing of a solid chemical compound which is not hygroscopic.

3. By the method employed, the admixture of salts, nitrogenous bodies and other impurities is prevented.

Results.—A mean of 10 determinations of a two years' old Bavarian white wine gave .766 per cent. glycerine. By Borgman's method, .807 per cent. glycerine.

Four determinations of a Bordeaux wine, seven years old, gave .720 per cent. glycerine, and by Borgman's method gave .819 per cent. glycerine.

Three determinations of Berlin White beer, gave .059 per cent. glycerine.

The slightly higher percentage found by Borgman's method is due to impurities in the final product. *H. W. W.*

Beer.—Two Acts, entitled "The Pure Beer Act" and "The Beer Adulteration Act" have been presented to the House of Commons during this year's session. The Analyst, 12, p. 99–100, gives the texts of these Acts and p. 103, the replies to a circular letter on the subject of beer sent out by the Council to the members of the Society of Public Analysts. The following papers were also presented.

An improved method of Detecting Quassia and certain other Hop-Substitutes in Beer. A. H. Allen, The Analyst, 12, p. 107.

Note on the composition of some preparations sold as Hop-Substitutes. A. H. Allen and W. Chattaway, loc. cit. 12, p. 112.

The following list of references to articles on the subject of Detection of Hop-Substitute in Beer are also given by A. H. Allen, loc. cit. 12, p. 98.

Systematic method of examining beer for bitter principles. Dragendorff, Jour. Ch. Soc. 27, 818.

Improved scheme of examining beer for bitter principles. Dragendorff, Jour. Chem. Soc. 43, 103. Year B'k Pharm. 1882, 120.

Useful scheme for detecting chief hop-substitutes. Wittstein, Jour. Ch. Soc. 29, 767.

Tabular scheme for separating hop-bitter, and detecting chief hop-substitutes, chiefly based on a method described by Enders. Allen Com. Org. Anal. 1, 97.

Method of detecting aloes, colocynth, wormwood, gentian, larch, fungus, scammony and jalap. Bach. Jour. Chem. Soc. **27**, 923 ; or far more perfectly abstracted in Year-Book Pharm. **1874**, 293.

Detection of Aloes in Beer. Bornträger Year-Book Pharm. **1880**, 140.

Presence of a natural substance in beer, giving reactions simulating certain of those produced by colchicine, gentian-bitter, etc. Jour. Chem. Soc. **31**, 325 ; **32**, 809.

Detection of noxious bitters in beer. Dupré Analyst. **8**, 40.

Reactions of picrotoxin. Year-Book Pharm. **1872**, 251. **1881**, 48. Chem. News, **39**, 264 ; **47**, 249 ; Jour. Chem. Soc. **40**, 286, 440 ; **43**, 412 ; **48**, 449 ; **50**, 284.

Isolation and characteristics of quassiin Christensen Jour., Chem. Soc. **42**, 1302 ; Phar. Jour. (3) **13**, 146 ; Adrian and Moreaux Jour. Chem. Soc. **46**, 908 ; Pharm. Jour. (3) **14**, 507. Oliveri and Denaro, Jour. Chem. Soc. **46**, 1192. Pharm. Jour. (3) **15**, 409.

A. L. COLBY.

New Pepper Adulterants.—(a)—*Poivrette or Pepperette*.—J. Campbell Brown, The Analyst, **12**, p. 23, 47, 72. Two varieties of this material are manufactured in Italy and are used to fraudulently increase the weight and bulk of pure pepper. Analysis:

	<i>White.</i>	<i>Black.</i>
Ash	1.33	2.47
Matters sol. by boiling in dilute acids . . .	38.52	34.55
Albuminous and other subs. soluble in alkali	14.08	17.66
Woody fibre insoluble in acid and alkali . .	48.48	47.69
Starch	none.	none.

White Poivrette is made by powdering cleaned, very pale, and perhaps partly bleached olive stones or precisely similar tissue.

Black Poivrette is the same material with a little black husks.

They can be distinguished in pepper by use of a microscope one-eighth objective in good daylight or a lower power (two-fifth) with the polarizer, analyzer and quartz plate, (previously

testing authentic samples to familiarize the eye). Also by boiling a portion of the sample in water to which a little caustic alkali has been added, dilute the thin mud with much water, allow to stand, and pour off the liquid from the remaining solid particles, and wash two or three times by decantation. The yellow particles are poivrette, the dark particles are husk. If any particles of bleached husk cells slightly resemble the poivrette, they may be distinguished by their softness and by the microscope.

(b)—*Long Pepper*, loc. cit. 12, p. 67. This is the fruit of *Chavica Roxburghi* and mostly derived from the wild plants occurring in India. Dirt is purposely gathered with it, samples showing 3-7 per cent. sand and clay. Analysis of Long Pepper, carefully cleaned by hand :

	Total Ash.	Sand and Ash insoluble in HCl.	Total matter Soluble in 10 per cent. HCl.	Starch and matters convertible into Sugar.	Albuminous matter soluble in Alkali.	Cellulose.	Extracted by Alcohol.	Extracted by Ether.	Total Nitrogen.
1	8.91	1.2	67.83	44.04	15.47	15.7	7.7	5.5	2.1
2	8.98	1.1	68.31	49.34	17.42	10.5	7.6	4.9	2.0
3	9.61	1.5	65.91	44.61	15.51	10.73	10.5	8.6	2.3

The presence of long pepper in good pepper may be determined by the following characters: Peculiar slaty color of the adulterated specimen; a distinct odor, best detected by warming the ethereal extract; an excessive percentage of sand; presence of pieces of fluffy woody fibre and husks differing from genuine pepper husks; the angular shape and large size of starch granules.

(c)—*Dhoura* loc. cit. 12, 89, known in Southern India as Cholum, in Bengal as Towari, in England as Great Millet or Turkish Millet. It is the grain of one of the cereal grasses, *Sorghum Vulgare*. Its presence can be detected by aid of a microscope. The influence of an admixture of sorghum with pepper, upon the analysis of the latter will be seen from the following analysis of sorghum grains.

<i>Composition of the Dried Sample.</i>	I.	II.
Ash	1.31	1.69
Sol. in 10 per cent. HCl	90.70	87.80
Starch	75.20	73.00
Albuminous matters sol. in caustic alkali . .	6.71	7.96
Cellulose	2.56	4.19
Alcoholic extract	10.36	7.96
Ethereal extract	10.10	7.30
Nitrogen	1.82	1.79

A. L. COLBY.

On Paraffin Scale Testing.—D. A. Sutherland, Jour. Soc. Chem. Ind. **6**, 123, 351. A discussion of the methods employed for the estimation of water, oil and dirt.

Soap Analysis.—F. M. Horn, Zeit. Chem. Ind. 1887, **2**, 85. The methods given in many text books which direct that the soap be dissolved in absolute alcohol and the NaCl, Na₂CO₃ and Na₂SO₄ be determined in the residue is misleading and gives erroneous results because these salts are slightly soluble in commercial anhydrous alcohol, which is never free from water, and because the soap itself contains 20 to 60 per cent. of water. Chlorine should be estimated by dissolving the soap in water and precipitating the fatty acids with nitric acid. The chlorine is estimated in the filtrate. Sodium carbonate may be determined by drying the soap, extracting with anhydrous alcohol (at least 97.5—98 per cent.) and estimating the Na₂CO₃ in the residue. A better method is to make a direct estimation of CO₂ in the soap. Sulphuric acid (Na₂SO₄) may also be estimated in the alcohol residue, or in the ash of the soap.

On the Estimation of Glycerine in Fats.—Hehner, The Analyst, **12**, 44. Saponify 3 grms. with alcoholic KOH, do not drive off the alcohol, but dilute to 200 c. c.; decompose soap with dil. H₂SO₄, filter and estimate insol. fatty acids as usual. Boil filtrate to 250 c. c., add 25 c. c. conc. H₂SO₄ (suitably diluted) and 50 c. c. standard K₂Cr₂O₇. Heat to near boiling for two hours, titrate back excess of K₂Cr₂O₇ with excess of (NH₄)₂Fe(SO₄)₂, and then the latter with decichro-

mate using K_2FeCy_6 as indicator. Calculate from chromate consumed, the per cent. of glycerine. In another paper (loc. cit. p. 65) the author proves that glycerine is not volatilized with aqueous vapor during concentration of a solution containing less than 50 per cent. Even with 73.8 per cent. the loss is insignificant. Solutions required:

1. $K_2Cr_2O_7$ —80 grms. 150 c. c. conc. H_2SO_4 to 1 liter, standardize with iron wire.

2. $(NH_4)_2Fe(SO_4)_2$ —120 grms. to 1 litre.

3. $K_2Cr_2O_7$ — $\frac{1}{10}$ above strength.

No. 2 is standardized upon No. 1. $K_2Cr_2O_7 \div 7.486 =$
glycerine. A. L. COLBY.

Beechi's Test for Cotton Seed Oil in Olive Oil.*—Dissolve one grain silver nitrate in 1 c. c. water and add 200 c. c. 96 per cent. alcohol and 20 c. c. ether. Mix 85 parts amylic alcohol with 15 parts rape seed oil. Take 10 c. c. of the suspected oil, add 1 c. c. of the $AgNO_3$ solution and then 8 to 10 c. c. of the mixture of rape seed oil and amylic alcohol. Shake well and heat on water bath for 5 to 10 minutes. A brownish color varying to black is produced if cotton seed oil be present.

A committee consisting of N. Peruzzie, N. Ridolfi and Prof. G. Roster of Florence was appointed to examine Beechi's test. After a thorough study of the subject they have pronounced it reliable. Cotton seed oil appears to be the only one that will give the brown coloration under the conditions named.

H. W. W.

A New Method for the Examination of Fats is proposed by Benedikt and Ulzer. Monatshefte fur Chemie 8, 41, (see also Benedikt, Zeit. Chem. Ind. 1887, 149). 100 gms. of the oil is boiled in a flask connected with an inverted condenser, with 70 gms. KOH dissolved in 50 c. c. water and 150 c. c. strong alcohol. The contents of the flask are poured into a large evaporating dish, diluted with a liter of water, acidified with dilute sulphuric acid and boiled until all the alcohol has

* Am. J. of Pharm., June, 1887; Pharm. J. and Transactions, July 16, 1887.

been driven off and the fatty acid swims on the surface as a perfectly clear layer. The fatty acid is then washed twice with hot water, separated from the remaining water in a separatory funnel and filtered at a temperature 20–30° above its melting point. 50 gms. of the fatty acid are then boiled for two hours with 40 gms. acetic anhydride in a flask with inverted condenser. The contents of the flask are emptied into a beaker holding 1 liter and boiled with 500–600 c. c. water. To prevent bumping a slow stream of CO₂ is passed through the mixture by a capillary tube leading nearly to the bottom of the beaker. The water is siphoned off and the boiling repeated three times with fresh water. The acetyl acid is then dried and filtered as before and two portions weighed out, the first of 4–5 gms. to determine the acid number, the second of 1–1.5 gms. to determine the saponification number.

“Acid number” and “saponification number” signify the number of milligrammes potassium hydroxide which are necessary for the neutralization and saponification of 1 gm. of the mixture of fatty acids.

The acid number is determined by dissolving in alcohol and titrating with $\frac{1}{2}$ normal soda lye with phenolphthalein as indicator.

The saponification number is determined by the method of Köttstorfer (Zeit. anal. Chem. 18, 199).

In this way the following acetyl numbers were obtained :

Peanut oil . . .	3.4	Walnut oil . . .	7.6
Cotton seed oil .	16.6	Olive oil . . .	4.7
Croton oil . . .	8.5	Peach oil . . .	6.4
Hemp oil . . .	7.5	Castor oil . . .	153.4
Linseed oil . .	8.5	Rape seed oil . .	6.3
Almond oil . .	5.8	Sesame oil . . .	11.5
Poppy seed oil .	13.1	Soluble Castor oil	62.2

The Analysis of Quinine.—O. Hesse, Pharm. Ztg., 1887, No. 37. This paper consists mainly of a review of the different methods for the analysis of quinine that have been published of late. The author says that the bisulphate method for the estimation of cinchonidine in sulphate of quinine, as

proposed by DeVrij and modified by Schäfer, gives results which are too high when but a small amount of cinchonidine is present, and too low when there is a large percentage of cinchonidine. He also says that by this method pure cinchonidine is not obtained, but a combination of 1 molecule of quinine and 2 molecules of cinchonidine. If, however, the author's modification of the method be used, satisfactory results can be obtained. It also has the advantage of furnishing the result with but a single operation.

The author describes the following modification of Paul's crystallization method :

5 grams of sulphate of quinine are dissolved in boiling water, the solution cooled and the mother liquor poured off from the separated crystals. These crystals are again dissolved in 120 c. c. of boiling water, the solution cooled and the crystals separated as before. This process is continued until all the cinchonidine is extracted from the crystals. If the sulphate of quinine contains 5 per cent. of cinchonidine three crystallizations are necessary ; for a sulphate containing 9 per cent. five are required. The mother liquors are united and evaporated almost to dryness. The residue is then dissolved in dilute sulphuric acid, the solution diluted to 20 c. c. with water, stirred with 16 c. c. of pure ether and an excess of ammonia added. The mixture is allowed to stand 24 hours and the separated crystals collected and weighed. Although these crystals contain some quinine the method is, on the whole, satisfactory, and the results agree very well with those obtained by the bisulphate method.

The chromate method of DeVrij is unsuited for the quantitative determination of cinchonidine, because of the tendency of the cinchonidine to pass into the chromate of quinine.

The oxalate method, proposed by Schäfer, gives results which are entirely too high ; thus a specimen of sulphate of quinine gave 5.09 per cent. of cinchonidine by the bisulphate method, 4.64 per cent. by the crystallization method, and 10.22 per cent. by the oxalate method. The oxalate of cinchonidine acts as a solvent upon the oxalate of quinine, and the mother

liquor upon evaporation gives crystals which contain a variable proportion of quinine. Schäfer himself has substituted for this method the tetrasulphate process, which he claims gives better results. *I. A. P.*

PHYSIOLOGY AND PATHOLOGY.

Determination of Uric Acid with Potassium Permanganate.—As the result of a study of this subject Blarez and Denigès conclude (*Comptes Rendus*, 104, 789) that it is necessary that

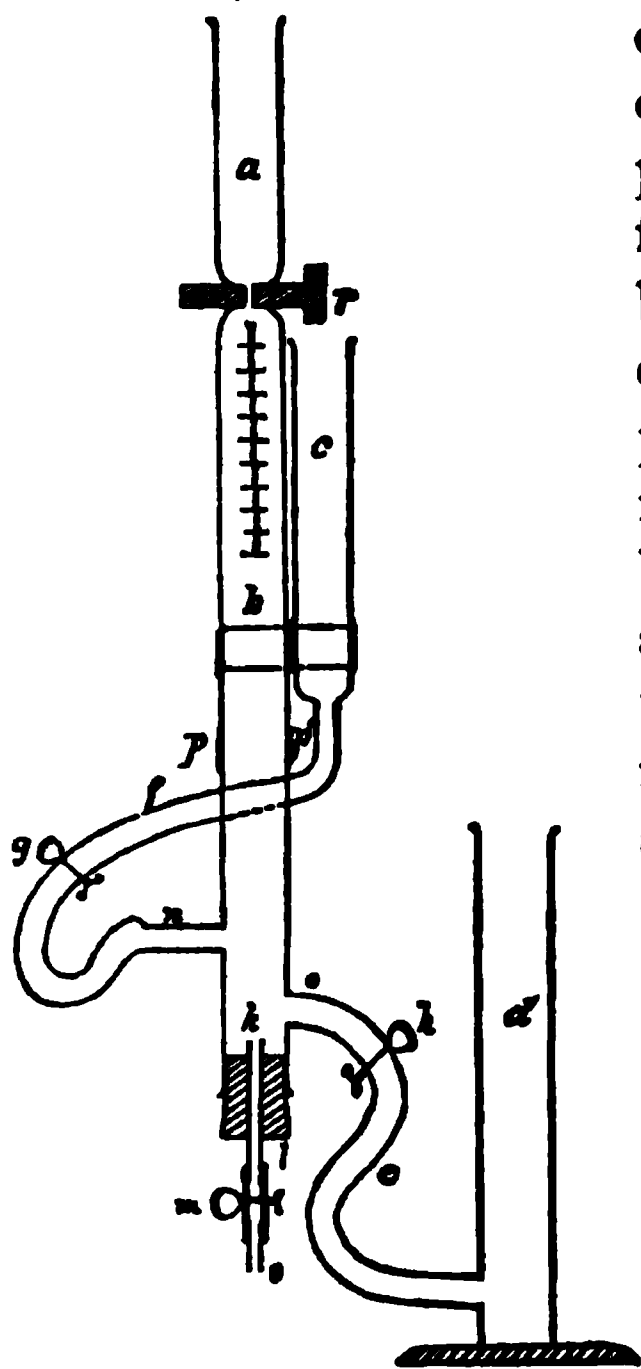
1. The dilution should be so great that at least 8000 parts water are present for every one part uric acid.
2. Not more than 0.1 gm. uric acid should be taken for a determination.
3. The quantity of free sulphuric acid present should be about 3.5 gms.

Quantitative Estimation of Lactic Acid.—R. Palm. *Zeit. anal. Chem.* 26, 33. When lactic acid is treated with lead acetate, and an alcoholic solution of ammonia added the lactic acid is completely precipitated as $3\text{PbO} \cdot 2(\text{C}_3\text{H}_5\text{O}_3)$. This precipitate is of constant composition and may be made use of in the quantitative determination of the acid.

The finely powdered substance in which lactic acid is to be estimated is extracted with ether, which dissolves only lactic acid, fat, and perhaps coloring matter. The ethereal solution is evaporated on the water bath and treated with water, which dissolves the acid, but leaves the fat undissolved. The filtered solution is now treated with lead acetate. If a precipitate forms this is filtered off and to the filtrate alcoholic ammonia is added as long as a precipitate forms. The precipitate is then brought on a filter and thoroughly washed with alcohol, in which it is insoluble. If the lactic acid is combined with a metal the substance is first treated with sulphuric acid and then extracted with ether. Any excess of sulphuric acid is precipitated when the lead acetate is added. The lactic acid

may be separated from the lead precipitate by passing sulphuretted hydrogen and extracting with ether. Very small amounts of lactic acid may be detected, if, instead of lead acetate, freshly precipitated lead hydroxide is used. In this case, however, the precipitate is not of constant composition.

A New Urinometer.—Dr. Georges Frutiger, Bull. soc. chim., 46 641. This apparatus, which is a modification of that of Yvon, is composed of a burette supplied at the lower end with two lateral tubulures on opposite sides and at different levels, as shown in the figure. The lower tubulure *o* is



connected by means of the stout caoutchouc tube *e*, supplied with a pinch-cock *h*, with the cylinder *d* filled with mercury. The upper tubulure *n* is connected by the caoutchouc tube *f*, supplied with the pinch-cock *g*, with the tube *c* which is bound to the burette by means of brass wire. The burette is closed at the bottom by a perforated cork through which passes a tube *k l* reaching to the level of *o* and closed at the bottom by a pinch-cock *m*.

To make a determination water is first poured into the tube *c*, the pinch-cock *g* opened and part of the water allowed to run into the burette. The cock *g* is now closed and *m* opened, allowing most of the water to run out at *s*, care being taken, however, that *k l* remains full of water, and that it contains no bubbles of air. The cylinder *d* is now raised by the hand and the mercury runs into the burette, filling it and part of the upper section *a*. The cock *r* is then closed and the cylinder replaced on the table. If there is any water on the surface of the mercury in *a*, it must be removed by means of filter paper. 1 c. c. of urine is now poured into *a* and the cock *r* slightly

opened, which allows the urine to descend into the burette ; *a* is washed with a little water and the washings added to the contents of the burette, The sodium hypobromite solution is next poured into *a* and run into the burette by slightly opening *r*, which is closed immediately. The nitrogen is disengaged and drives out the mercury into *d*. When all action has ceased, the remainder of the mercury is driven out by pouring water into *a* and slightly opening *r* ; the water descends and replaces the mercury. The hypobromite solution is now removed by pouring more water into *a*, slightly opening *r* and then opening the waste-cock *m*. The solution runs out and is replaced by the pure water from *a*. To make the reading, *r* and *m* being closed, the pinch-cock *g* is opened and the levels in *b* and *c* adjusted by adding water to *c* or running it out from *h* through *m*. The quantity of mercury necessary is 500 grams.

I. A. P.

Method for Detecting Small Quantities of Trypsin.—H. Leo. Pflüger's, Arch. f. Phys. **39**, 246. If a solution containing trypsin is allowed to remain in contact with particles of fibrin for 18–22 hours the solution then poured off, 4 c. c. 1 per cent. soda solution added and the mixture allowed to stand at blood heat for five hours the fibrin dissolves more or less completely according to the amount of trypsin present. If on adding a few drops of a dilute alkaline copper solution the liquid takes a reddish or violet color, trypsin is present. In this way it is possible to detect the amount of trypsin contained in 1 drop of a solution made by treating 177 gms. pancreas with 200 c. c. glycerine.

The Detection of Small Quantities of Albumenoids.—R. Palm, Zeit. anal. Chem. **26**, 35. In an alkaline solution Schlippe's salt (sodium sulphantimoniate) gives a yellow precipitate. Solutions of potassium antimoniate, and of sodium nitroprusside acidified with acetic acid also precipitate albumenoids. The tests for albumenoids now in use are much more delicate when an alcoholic solution of the reagent, to which a little ether (10 per cent.) has been added, is used. In this case the precipitate obtained is not dissolved by an

excess of the reagent. Alcoholic solutions of the following salts are especially recommended :

(1) Ferric acetate, which has been made basic by warming with freshly precipitated ferric hydroxide. When warmed with a solution of an albumenoid this causes complete precipitation.

(2) Basic cupric acetate. The precipitate obtained may be dissolved in acetic or lactic acid, a little sodium hydroxide added and the solution boiled ; the albumenoid then causes the reduction of the copper salt.

(3) Lead acetate or chloride. This precipitate is white and may be further tested by the Adamkiewicz method (sulphuric and glacial acetic acids).

(4) The most delicate reagent is a solution of freshly precipitated lead hydroxide in water. By this reagent it is possible to detect one part in 500,000 water, especially if a little alcohol is added. The precipitate may also be further tested by the Adamkiewicz reaction.

AGRICULTURAL ANALYSIS.

EDITED BY H. W. WILEY.

Moisture and Free Acids in Superphosphates.—John Ruffle* has contributed an interesting study on the above subjects.

The loss of moisture, dried to constant weight, at various temperatures varied in one sample from 12.92 per cent. at 100 to 120° F., to 17.93 per cent. at 300° F.

Drying at the same temperature (212° F.) for different periods showed a variation of from 9.97 per cent. for 30 minutes to 17.15 per cent. for seven hours. The fertilizer dried in its natural state at 212° F., showed a much greater loss of moisture than when previously rubbed to a fine paste in a mortar. Drying for any considerable period at 212°F., also

*J. Soc. Chem. Industry, May 31, 1887.

affected the percentage of soluble P_2O_5 in the sample, the loss amounting in one instance to .60 per cent.

When dried over H_2SO_4 at ordinary temperatures this loss does not take place, but the time required for complete desiccation, viz: 15 to 18 days, renders this method impracticable.

The soluble P_2O_5 was shown by the experiments of Ruffle to exist chiefly in a free state and not as mono-calcium salt as is generally supposed.

Having tried all the common methods of drying, the process finally adopted was dessication over dry $CaCl_2$ in a vacuum.

A sample of Carolina superphosphate treated in this way gave on February 1, 14.38, 14.42 per cent. H_2O ; March 23, 13.57, 13.55 per cent. H_2O ; April 25, 12.86, 12.90 per cent. H_2O .

This gradual loss of free water is doubtless due to the gradual absorption of the water by $CaSO_4$ as it passes into the state of monohydration. The estimation is made by placing 2 to 5 grams of the sample in a watch glass over $CaCl_2$ for 24 hours in a vacuum produced by a good air pump.

To determine the distribution of water among the various constituents of the fertilizer is a difficult problem, but it may be done approximately as follows:

- (a). From the soluble P_2O_5 and CaO found in filtrate calculate the per cent. of mono-calcium phosphate.
- (b). The rest of the soluble P_2O_5 calculate as free acid.
- (c). From the insoluble P_2O_5 calculate the $Ca_3(PO_4)_2$;
- (d). The whole of the H_2SO_4 calculate into $CaSO_4$ combined with one molecule H_2O .

Complete analyses show that the water removed in this way by $CaCl_2$ is practically the uncombined water of the samples, while it is equally true that drying at 212° to constant weight drives off a considerable amount of combined water. Only one molecule of H_2O has been assigned to $CaSO_4$ in the work done by Mr. Ruffle, because of all the various experiments tried by drying in presence of calcium chloride, sodium hydrate, etc. none left sufficient water in the manure to supply the $CaSO_4$ with more than one molecule.

The discussion of Mr. Ruffle's paper is given in No. 6, Vol. VI of the Journal of the Society of Chemical Industry.

The value of the method was admitted on all sides and it seems to be a happy settlement of the unsatisfactory attempts which have been made heretofore to determine moisture in superphosphates.

Analysis of Superphosphates.—The true composition of a superphosphate, not ammoniated, is to be found according to Ruffle, as follows :*

- (a) Estimate moisture by calcium chloride method in vacuo.
- (b) Soluble P_2O_5 by direct determination.
- (c) Insoluble P_2O_5 by direct calculation from the amount of insoluble phosphoric acid after evaporation to dryness with HCl and resolution with HCl.
- (d). $CaSO_4$. Determine the whole SO_3 present and calculate into $CaSO_4$ (anhydrous).
- (e) Sand, etc. Matters insoluble after above evaporation to dryness with HCl.
- (f) Combined water and organic matters, etc.
- (g) Alkalies, magnesia.

A comparison of the new and old statements of analyses is also given.

Carolina Superphosphate.

	<i>Old.</i>		<i>New.</i>
Loss at 100° C.			
Moisture	20.22 per ct.		13.17 per ct.
Combined water and organ-			
ic matter	4.51 "		21.46 "
Biphosphate	19.07 "	sol. P_2O_5	13.68 "
Insoluble phosphate98 "		.98 "
$CaSO_4$	36.64 "		44.88 "
Alkalies, etc.	12.85 "		12.85 "
Insoluble sand, etc.	5.83 "		5.83 "

When ammoniated superphosphates are under examination the whole of the H_2SO_4 found, cannot of course, be calculated into $CaSO_4$. A part of it is combined with the ammonia. In this case the total CaO is to be determined and then the CaO

* Jour. Soc. Chem. Industry, July 30, 1887.

combined as insoluble phosphate. The remainder is calculated to CaSO_4 .

[NOTE.—Mr. Ruffle appears to have proved the correctness of his assumption that nearly the whole of the soluble P_2O_5 in a superphosphate exists as a free acid when the proper quantities of H_2SO_4 have been used in the mixture. If an insufficient quantity be used, it is fair to presume that a portion of the soluble P_2O_5 may exist as a monocalcium salt. On the other hand if an excess of H_2SO_4 be used the rule to calculate all the H_2SO_4 as CaSO_4 would give too large a quantity of CaO].

Butter Analyses.—F. W. A. Woll* gives the results of a large number of analyses of butters and butter substitutes. The specific gravity of the filtered fats was made at 37.76° and the fats examined by the method of Koettstorfer and Reichert. The specific gravity of the genuine butter was found to vary between .911 and .914. The milligrams potash per gram of fat varied from 221.4 to 232.4.

Beef fat showed an average specific gravity of .9037 and required 193.4 grams potash for one gram of fat. Lard has a mean specific gravity of .9053 and requires for each gram of fat 193.3 mgs. of potash. The author says the specific gravity and Koettstorfer's or Reichert's methods, either singly or in combination, are decisive in detecting butter adulterations.

Various artificial butters were made by the author from butter and "oleo" and "neutral" whose behavior with the various reagents was previously determined. The estimation of the percentage of genuine butter in the mixtures agreed fairly well with the amounts actually present,

[NOTE.—It cannot be inferred from the above that an adulteration of 10, or even 20 per cent. in butter can be positively determined by any of the methods given. For instance, a genuine butter by Reichert's test may show from 12 to 16 c. c. of one-tenth N. alkali. The numbers obtained by Koettstorfer's method and the specific gravity numbers also vary greatly. An admixture of 20 per cent. "oleo" or "neutral" with a butter showing 16 by Reichert's method would probably es-

*American Chemical Journal Vol. 9, No. 1.

cape detection either by specific gravity, Reichert or Koettstorfer].

Reichert's Method of Butter Analysis.—Cornwall and Wallace* have made experiments to determine the limits for pure butter of one-tenth alkali in Reichert's method.

80 samples of pure butter showed a mean of 13.68 c. c. Each sample was made from the milk of a single cow. The authors consider 12.5 c. c. as too high for the minimum for pure butter. In one instance they found only 11.3 c. c. The maximum number obtained was 15.1 c. c.

Examination of Coloring Matter in Butter.—J. H. Stebbins, Jour. Amer. Chem. Soc. 9, 41. "50 gms. of butter fat, freed from curd, salt and water are weighed out into a small, narrow beaker. The fat is then melted on a steam bath, and into it is stirred 5 or 10 gms. of finely pulverized fullers earth. The mixture should now be thoroughly stirred for 2 or 3 minutes and then allowed to remain upon the steam bath until the earth has fully settled. As much of the clear fat as possible is now poured off into another beaker without disturbing the sediment. To the sediment remaining in the first beaker is added 20 c. c. benzole: the mixture is thoroughly stirred with a glass rod, the earth allowed to settle, and the benzole poured off into a clean filter.

This washing with benzole is repeated until a few drops evaporated upon a watch glass, leave no fatty residue.

The filter paper is now rinsed with a little more benzole and all the filtrates united in a flask. If carotene has been used for coloring the butter it will be contained in the benzole, and may be tested for in the usual manner. Carotene is very easily soluble in benzole and very difficultly soluble in alcohol. There will, therefore, be no trouble in totally extracting it from the earthy sediment. The earthy sediment, freed from fat and carotene, is now heated upon the water bath until the last traces of benzole have been driven off. It is then boiled out 3 times with about 20 c. c. of 94 per cent alcohol. The alcoholic extracts are filtered into a tared evaporating dish,

*Zeit. anal. Chem. 26, p. 317.

and the alcohol is then driven off. The residue left in the dish, composed of curcumine or annatto, or possibly both, is dried to constant weight at 100° C, weighed and then tested colorimetrically in the usual manner."

Curcumine and annatto are nearly insoluble in benzole, but are, on the contrary, very easily soluble in alcohol. It is therefore not likely that any of these coloring matters will be extracted by the benzole in the first operation.

A. R. Leeds, *Ibid.*, 76, has published another method for the estimation of these coloring matters as follows: 100 gms. of the sample are dissolved in 300 c. c. light petroleum, washed with 100 c. c. of water in portions in a separatory funnel, and then allowed to stand for 15–20 hours in a cold place or surrounded by ice. This causes the separation of stearine. The solution is decanted from the stearine and shaken with 50 c. c. $\frac{1}{10}$ potash solution which dissolves out the coloring matter. The potash solution is drawn out, made faintly acid with dilute hydrochloric acid and the coloring matter filtered off, washed with cold water and dried on a weighed filter. The coloring matter is always accompanied by a small amount of fatty acid from the action of the potash solution on the fat. The ethereal solution of the pure fats have, according to the author, a slight yellow color which cannot be removed by treatment with alkali. From 5 c. c. of Wells, Richardson & Co's butter color 0.048 gms. coloring matter were obtained. It appears to be annatto dissolved in cotton seed oil. Hanson's contained 2.66 per cent. annatto dissolved in cotton seed oil and Fargo's 3.10 per cent. of annatto dissolved in cotton seed oil.

Another method is described by E. W. Martin*, as follows: A mixture is prepared of 15 parts methyl alcohol and 2 parts carbon disulphide. 25 c. c. of this solution is well shaken in a test-tube with 5 gms. of the fat to be examined. The carbon disulphide dissolves the fat and separates at the bottom of the tube while the methyl alcohol dissolves the coloring matter. Instead of methyl alcohol, ether, acetone, ethyl alcohol, etc., may be used.

E. H.

*The Analyst, 19, 79.

Estimation of CO₂ in Soils.—Paul de Mondésir* has described an apparatus for determining carbonates in arable soils.

The object of the apparatus is to estimate the quantity of carbonate in a condition to favor plant growth and not to determine the whole quantity present.

The apparatus to be used consists of a flask of from 300 c. c. to 1000 c. c. capacity with a neck near the bottom. Into this neck is fitted by a stopper a manometric tube which is bent upwards near the stopper at an angle a little greater than 90°, so that it can be fixed in some way to the upper part of the flask. This tube on the end entering the flask (a Mariotte's bottle is well suited for the purpose) carries a rubber pouch. The toy balloons sold on the streets can be used. This manometric tube should have an internal diameter of from 2 to 3 mm. and a length of .7 to 1 m. It should be fastened to the top of the flask so that on shaking the apparatus, it is not displaced. The apparatus is calibrated as follows :

The rubber bag, previously freed from air, is filled with water until the level of the water is above the elbow of the manometric tube. A certain quantity of water, which should be equal for all subsequent operations is then placed in the flask. This volume should be about one-quarter of the content of the flask.

80 or 400 mg., according to the size of the apparatus, pure precipitated CaCO₃ are then added to the water. The flask is then stoppered and well shaken.

A quantity of finely pulverized tartaric acid, at least three times the weight of CaCO₃ taken is next weighed out ; the acid is added to the mixture in the flask, the stopper firmly inserted and the height of the water in the tube marked. The flask is then shaken for about a minute, by which time the carbonate is all decomposed. The increase in tension, due to the liberation of CO₂ is shown at once by a rise of the water in the tube. The manometric tube is to be furnished with a stopper which is to be inserted when the apparatus is shaken or when it is cleaned. By this means the quantity of water remaining

* Annales de la Science Agronomique, 1886, Vol. II, 2nd part.

in the rubber apparatus is always the same. The quantity of water in the rubber bulb should be two or three times greater than the total interior capacity of the tube.

In filling the tube water is first poured into the flask to press out the air. If a few bubbles of air remain in the tube or rubber bag, they will not interfere with the work unless they escape. Having determined the use of water in the tube due to a given weight of $CaCO_3$, the flask is cleaned, and refilled with the same quantity of distilled water.

From 75 to 150 grams of soil, according to its richness in carbonate are now added, the tartaric acid poured in, and the height of the water in the tube noted. The flask is then well shaken. To prevent a too rapid action of the acid before the water level can be read, it is well to wrap it in paper.

All operations should be conducted at the same temperature as originally noted in gauging the apparatus, and of course, the same barometric pressure ought to be secured. Methods for correction for variations in pressure and temperature are given.

[NOTE.—The apparatus described is not intended to give the total quantity of carbonate in a soil. While not capable of exact determination, it is extremely ingenious and I think can be used to advantage in roughly estimating the lime carbonate of a soil in a state of fineness suitable for plant use.]

Testing Skim Milk by the Lactocrite.—Faber* shows that the percentage of fat in skim milk when determined by the lactocrite is too low. This deficiency in ordinary skim milk amounts to about 0.1 per cent. while in those milks where the cream has been more carefully removed it may reach .2 per cent. Separated milk containing less than .3 per cent. cannot be tested with the lactocrite.

The Agricultural Value of Reverted P_2O_5 .†.—Experiments showed that the superphosphate was more active than the insoluble form or the reverted. The reverted acid was obtained by leaching a superphosphate rich in reverted. 22.5 kilos per

* Analyst, July 1887, p. 130.

† J. Jaffre Bul. Soc. Chim. Vol. 47, p. 312; Chem. Central B. 23, April, 1887, p. 417.

hectare were used. In some kinds of soils, however, the author admits that the superphosphate can be advantageously replaced with some insoluble forms of the acid, but in general the reverse is the case.

Composition of Milk from Cows fed on Brewers' Grains.*—
The dried grains had a mean composition of

Protein	22.7 per cent.
Fat	7.8 “
Nitrogen free extract	39.4 “

The milk from cows fed on the above had the following composition :

Water	85.37 per cent.
Albuminoids	4.70 “
Fat	3.71 “
Milk Sugar	5.42 “
Ash80 “

The total solids in the above milk are considerably higher than in average normal milk.

[NOTE.—A sample of brewers' grains lately examined in our laboratory had the following composition :

Albuminoids	21.97 per cent.
Fat	5.66 “
Crude fibre	8.81 “
Starch, sugar, gum, digestible fibre, &c. (by difference) . . .	51.37 “
Ash	4.33 “
Moisture	7.86 “]

Influence of Freezing on Milk.†—By the first named observer the following numbers are given :

<i>Original Milk.</i>			<i>Ice Portions.</i>		
	Sp. Gr.	Total Solids.		Sp. Gr.	Total Solids. Fat.
Quickly frozen . . .	1.031	11.37	2.89	1.0279	9.68 2.37
Slowly frozen } with stirring, }	1.0302	11.87	2.92	1.0234	6.43 0.54

* J. Schiller Zeit. für Spiritus industrie, Vol. 10, No, 3, p 19.
† O. Hanzhold, Milchzeitung, Vol. 15, No. 27, p. 461 ; and Kaiser & Schmeider, op. cit. Vol. 16, No. 11, p. 197.

Liquid Portion.

	Sp. Gr.	Total Solids.	Fat.
Quickly frozen	1.0337	12.72	3.89
Slowly frozen with stirring	1.0338	11.37	2.41

By the second named observers the following numbers were obtained. The sample to which some cream had been added, was frozen until the ice was approximately of the same volume as the liquid portion.

	<i>Original Milk.</i>	<i>Liquid Part.</i>	<i>Ice.</i>
Sp. Gr.	1.029	1.040	1.015
Casein	3.18 per cent.	4.42 per cent.	2.57 per cent.
Fat	7.40	4.11	10.10
Milk sugar	3.90	5.95	2.14
Ash	0.59	0.97	0.50
Total solids	25.07	15.45	25.31
Water	84.93	84.55	84.69

The data in the two sets of analyses are somewhat contradictory.

In the first table it is seen that the ice portion contained less fat than the liquid part, while just the contrary is true of the second set of analyses.

[NOTE.—So much depends here on the method and extent of the freezing that I do not see much of value in such studies.]

Determination of Oxalic Acid in Plants.—Berthelot and André (Annales de Chim. et de Pharm. March, 1887, pp. 289 et seq). describe the methods of analysis used in their researches on the occurrence of oxalic acid in plants.

The different parts of the plant which are to be examined, are separated from each other, weighed as quickly as possible and then rubbed up in a mortar. The material is now thrown into a porcelain dish, sufficient water is added and this is heated gradually until near the boiling point, for one hour. It is then left to macerate for 24 hours. The water is then decanted and filtered, the residue treated with a fresh quantity of water. After a second filtration the residue is pressed in a cloth. The filtrate is treated with dilute hydrochloric acid, carried to ebullition and again filtered. The oxalic acid is then precipitated with lime. The weight of the oxalate ob-

tained gives the quantity of free oxalic and soluble oxalates in the plant.

The total oxalic acid in the plant is obtained as follows :

The extraction is made upon another sample of the plant taken under the same conditions as above.

The extraction of the total oxalic acid is accomplished in the same manner as was used for the soluble, except that to the water of maceration is added 20–30 c. c. of strong hydrochloric acid to each 40 c. c. water and 100 gms. of the plants. Upon the addition of ammonia to the filtrate the oxalate of calcium is precipitated in a uniform state and mixed with various other salts. It is necessary to separate the insoluble salts formed by the other organic acids which may be present, such as tartaric and citric, as also mineral acids, such as phosphoric and sulphuric.

For this purpose dissolved boric acid is added in excess (50 c. c. of a concentrated solution). The presence of this acid with the aid of the ammonium chloride present causes the formation of certain special double salts. These prevent the precipitation of tartrates, citrates, paratartrates, &c., and further cause the solution of those salts already precipitated. This action of boric acid has been verified by special quantitative studies.

Without the employment of boric acid and ammonium chloride the determination of the oxalic acid is likely to be inexact.

The solution is now made strongly acid with acetic acid which dissolves any carbonates which may be present. After the addition of some acetate of lime the mixture is heated for an hour but without boiling. The precipitated oxalate is collected on a filter and washed but it is still too impure to be weighed. The salt is dissolved in hydrochloric acid, some more boric acid added and then reprecipitated by ammonia. This process is repeated two or three times.

To avoid the presence of filter paper, the final filtration is made on Parmichael's plan of upward filtration by a perforated glass bulb covered with a film of asbestos. (It appears that these distinguished chemists are not familiar with the princi-

ple of the Gooch crucible and they even claim the above device of Carmichael as original.)

The resulting oxalate is then weighed as such, or according to the directions given, changed into sulphate and weighed in that form. .

The authors, however, prefer to estimate it by measuring the volume of carbonic oxide which it affords when decomposed by hot sulphuric acid.

To the flask containing the washed precipitate and a few c. c. of water are added 15 c. c. strong sulphuric acid. This flask is also connected with a CO_2 generator by which a current of this gas can be conducted through it. Above is a condenser so that all the steam which is formed is returned to the flask, thus keeping the volume of liquid in the flask constant.

Before beginning the decomposition of the oxalate the air is driven out of the flask by the carbon dioxide. As soon as this is done the current of CO_2 is shut off and the oxalate decomposed gradually by the aid of heat. The gas is collected over mercury in a test tube containing a concentrated solution of potash. At the end of the reaction the current of CO_2 is again passed until all the CO has been collected in the test-tube.

After the absorption of the CO_2 the gas is transferred to another tube and dried with solid potash. The volume of the residual gas (CO) is then corrected for temperature and pressure, and the weight of oxalic acid calculated. The authors give a large number of studies to show the relative proportions of water and H_2SO_4 and the time necessary to secure a complete decomposition of the oxalate.

They show that the decomposition takes place best when the dilution of the acid is least. Hence very little water should be left in the flask before the addition of the H_2SO_4 .

The action of H_2SO_4 in similar conditions on formic, citric, tartaric, racemic and malic acids and on glucose and filter paper is also noted. All of these bodies give off CO when treated as described, and hence all must be absent if the exact determination of the oxalic acid is to be secured.

[NOTE.—It is not apparent that this method of estimating

oxalate of calcium has any advantage in the way of accuracy over the ordinary methods of weighing it as carbonate or oxide. If the method could be applied to the impure oxalates as they exist in the plant then its value would be great. But the oxalate must be in its purest state before the decomposition is made, and in that state could be much better estimated by the usual methods.]

Oxalic Acid in Plants of Different Periods of Growth.—Berthelot and André have applied the methods above indicated to the determination of the quantity of oxalic acid in plants at the different stages of growth.

Without giving the results for all the plants investigated, it will nevertheless be of interest to give the studies of the one plant which we usually associate with the idea of oxalic acid, viz : the *Rumex acetosa*, or Sorrel.

In the seed of this plant there was found 0.05 per cent. $\text{H}_2\text{C}_2\text{O}_4$.

On the 8th of June, at the beginning of vegetation, the plant contained 13.9 per cent. $\text{H}_2\text{C}_2\text{O}_4$, or nearly one-seventh of its entire weight.

On the 26th of June, vegetation active, the oxalic acid in the plant was distributed as follows :

	<i>Sol. acid per cent.</i>	<i>Insoluble acid per cent.</i>	<i>Total per cent.</i>
Roots.	trace	4.25	4.25
Stems and petioles . .	2.30	8.03	10.33
Leaves	6.70	5.27	12.07
	<hr/>	<hr/>	<hr/>
Whole plant	4.31	5.97	10.28

On the 27th of September the analyses gave the following figures :

	<i>Sol. acid per cent.</i>	<i>Insoluble acid per cent.</i>	<i>Total per cent.</i>
Roots.	0.05	1.65	1.70
Stems and petioles . .	4.21	1.63	5.84
Leaves	3.79	0.67	4.46
	<hr/>	<hr/>	<hr/>
Whole plant	1.65	1.57	3.16

Taking into consideration the weight of the plant, it was

found that while the total amount of oxalic acid in the plant continued to increase during its entire life-time, the relative weight diminished from the beginning of vegetation until the plant reached full maturity. The proportionate weight of the acid present in September was only a third of that found in June and a fourth of that noted at the commencement of vegetation. This decrease was found especially in the roots and foliage. The roots contained only insoluble oxalates. The estimation of the mineral constituents of the plants shows lime in excess of acid in the roots. In the petioles and stems the lime is not sufficient to saturate the acid, while the foliage presents this curious circumstance that it is very rich, both in soluble oxalates and in lime.

P₂O₅. Estimation of by Decomposition of the Phospho Molybdate Precipitate with an Alkali.—Laible* condemns the method proposed by Isbert† because the quantity of ammonia in the compound is not constant. The analytical operations were conducted in different ways but all led to the same result.

*Chem. Zeit. Vol. 11, p. 186; Chem. Central. B. 30th April 1887, p. 439.

†This Journal, Vol. 1, p. 349.

NEW BOOKS.

REVUE INTERNATIONALE SCIENTIFIQUE ET POPULAIRE DES FALSIFICATIONS DES DENREES ALIMENTAIRES.

This is the first number of volume 1 of this Journal, which proposes to discuss the adulteration of foods as practiced in all countries, the methods of chemical and microscopical analysis for the detection of such adulterations, and the laws against adulterations. It is proposed that the articles be published in three languages—French, German and English. The articles in the present number are in two languages—French and German—with one or two shorter ones in French and English. The editor-in-chief is Prof. Hamel Roos of Amsterdam, who has a long list of distinguished collaborators, among whom we find the names of such men as König, Foster, Soyka and

Hilyer. These are evidences that the journal will be worth the small subscription of 8 francs and much more. In the present number König gives his method of making analyses of the commercial peptones, and Caro of Spain gives a review of the measures taken against food adulteration in his country. We hope that the Review will be liberally sustained. v. c. v.

"THE ELEMENTS OF QUALITATIVE ANALYSIS, by Wm. A. Noyes, Terre Haute, Ind. 77 pages cloth. Published by the author, mailing price 60 cents. A review of a book on Qualitative Analysis is unnecessary. Those who wish to use such a book should examine it themselves to see whether it is adapted to their needs. It is only necessary to say here, that Prof. Noyes' book is well worth careful examination. His explanations are short and to the point and are not likely to leave the student in a hopeless muddle. What is needed most in such a book is explicit directions, and these are given; explanations must necessarily, in most cases, be left to the teacher. E. H.

FOURTH ANNUAL REPORT OF THE AGRICULTURAL EXPERIMENT STATION OF THE UNIVERSITY OF WISCONSIN FOR THE YEAR 1886. MADISON, WIS. This report contains papers as follows: Report on the various crops grown in 1886. Dehorning cattle. Feeding waste products of the dairy. Ensilage versus fodder corn. The value of manure from stock on the farm. Experiments with corn fodder. Cost of making beef from dairy stock, will it pay to raise the calves of dairy cows for beef. Cooked versus uncooked food for swine. Feeding for fat and for lean. The foregoing papers by W. A. Henry. Feeding standards and composition of feeding stuffs. Analyses of feeding stuffs. Feeding value of roller bran. On the influence of the nutritive ratio upon milk production. Analyses of milk of different breeds of cows and Analyses of Fertilizers and other products by H. P. Armsby. Methods of Butter Analysis and Notes on Baron Hübl's method of analysis of fats by F. W. A. Woll. The paper on feeding for fat and for lean is illustrated with three lithographic plates and is an interesting and valuable article. E. H.

AN EPHEMERIS OF MATERIA MEDICA, PHARMACY, THERAPEUTICS AND COLLATERAL INFORMATION BY EDWARD R. SQUIBB, EDWARD H. SQUIBB AND CHARLES F. SQUIBB. VOL. 3, No. 2. OCT. 1887. Our space is too short to give titles of the articles contained in this number. Abstracts of several will appear in the next number of the Journal. The Ephemeris has always been well worth reading and the present number is fully up to its predecessors in interest. E. H.

PAMPHLETS RECEIVED: The Methods Employed in the Analysis of the Iron Ores. [Collected for the Tenth Census U. S.] By A. A. Blair.

—Studies in the Mica Group. By F. W. Clarke. Reprinted from the American Journal of Science, Aug. 1887.

—Plant Analysis as an Applied Science. By Helen C. DeS. Abbott. Reprinted from the Journal of the Franklin Institute.

—Wool : Its Structure and Strength, by Wm. McMurtrie, E. M., Ph. D. From the thirteenth Report of the Board of Trustees of the University of Illinois, Urbana, Champaign Co., Ill.

—Plant Chemistry as Illustrated in the Production of Sugar from Sorghum, by Helen C. DeS. Abbott.

—An Outline of the Structural, Surface and Economical Geology of Northern Georgia. By James A. Burns, Ph. D., Atlanta, Ga.

—Notes on the Literature of Explosives, No. XIV. By Chas. E. Munroe. Reprinted from Proc. U. S. N. I.

—Report of the Committee [A. A. A. S.] on Indexing Chemical Literature.

NOTES.

—Prof. H. B. Cornwall writes to the *Chemical News* that he has recently met with a butterine which gave only very a faint annato reaction from the filtered fat, while the decanted, unfiltered fat gave a fine reaction. In this case it was evident

that the annatto had been employed in the solid state. (See this Journal 1, 347.)

—Dr. Clemm has recently patented a process in Germany, England, France, the United States, etc., for destroying phylloxera and other parasites injurious to plants. This consists in incorporating with the soil, turf saturated with acid (nitric, sulphuric or phosphoric), and afterwards, a sulphide or carbonate (potassium, sulphide or carbonate). This results in the formation of a salt of potash which acts as a fertilizer and sulphuretted hydrogen or carbon dioxide which destroys the phylloxera. Even field mice and Colorado potato beetles may be destroyed in this way. Dr. G. Krause, editor of the *Chemiker Zeitung*, Cöthen, Germany, informs the Editor that he will furnish small amounts of material without cost to those who wish to try the plan.

—Prof. Curtman finds that the amount of lead contained in the St. Louis water varies with the amount of suspended sand contained in it. The sand in passing rapidly through the pipe rubs off small particles of metallic lead which can be seen when the sediment is examined with the microscope. (Pharm. Rund. 5, 238.)

—The oil of *Myristica Sebifera*, a species of nutmeg growing in Guatemala, is to be extracted and exported to the United States. The supply is abundant and the only expense is that of gathering the beans. It is proposed to use the oil as a substitute for lard and butter. See Chem. News, 56, 133.

—NECROLOGY.—On July 17th, L. G. de Koninck, formerly Professor of Paleontology and Chemistry in the University of Lüttich.

—On September 4th, of heart disease, Dr. J. Skalweit, Editor of the *Repertorium der Analytischen Chemie*.

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